THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

NOTE ON THE REMOVAL OF ARSENIC FROM HYDROCHLORIC ACID FOR USE IN THE MARSH-BERZELIUS METHOD.

By Arthur R. Ling, F.I.C., and Theodore Rendle.

(Read at the Meeting, December 6, 1905.)

It is a well-known fact that hydrochloric acid sufficiently free from arsenic for use in the Marsh-Berzelius method cannot be purchased, nor is this surprising, seeing that the acid acts on the glass bottle in which it is stored, and glass usually contains arsenic. Even the purest hydrochloric acid obtainable in commerce has therefore to be submitted to some preliminary purification before it can be used for any method of determining arsenic.

The Joint Committee of the Society of Chemical Industry and of the Society of Public Analysts recommended a method for the purification of hydrochloric acid which depends in principle on the fact first pointed out by Rohmer (*Ber.*, 1901, xxxiv., 31), that the presence of hydrogen bromide expedites the volatilization of arsenious oxide from a solution when it is distilled in a current of hydrogen chloride and sulphur dioxide. The Joint Committee's method consists in diluting the hydrochloric acid to be purified with water until it has a specific gravity of 1·10, adding about 5 c.c. per litre of bromine, and decolorizing the yellow solution with an excess of sulphurous acid. The acid, after standing for at least twelve hours, is boiled or distilled. The whole of the arsenic is contained in the first portion of the acid (one-fifth of the whole) which passes over.

One of us employed this method regularly until about two years ago, when it was discarded in favour of distillation with metallic copper (the Reinsch method). The reasons for rejecting the Joint Committee's method were threefold. In the first place, it was found very difficult to employ the method successfully with commercial hydrochloric acid. The Committee's instructions are that acid purchased as "pure" is to be treated. In the second place, the yield of arsenic-free acid seldom, in practice, exceeds three-fifths of that originally taken; and, lastly, the method is a lengthy one. The Reinsch method was carried out under conditions devised by Dr. L. T. Thorne, who very kindly gave us complete details of his *modus operandi*. In our experience, Dr. Thorne's method is superior to that of the Joint Committee, as it can be used for the purification of commercial hydrochloric acid. When, however, the acid contains much arsenic the method is extremely slow.

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The method of separation of arsenic from non-volatile substances by distillation in presence of hydrochloric acid was considerably simplified and rendered much more exact by Emil Fischer's proposal (*Ber.*, 1880, xiii., 1778) to add ferrous chloride as a reducing agent before distillation. When, however, the residue as well as the distillate has to be examined, the addition of iron is obviously undesirable. In view of this, various other reducing agents have from time to time been proposed, and C. Friedheim and P. Michaelis (*Ber.*, 1895, xxviii., 1414) proposed methyl alcohol for this purpose.

A few months ago H. Cantoni and J. Chautems (*Arch. Sc. phys. nat. Geneve* (4), xix., 364) stated that when a current of air is passed through a solution of arsenious oxide in hydrochloric acid to which methyl alcohol has been added at the ordinary temperature the arsenic is volatilized, probably in the form of the ester methyl arsenite. As soon as this work became known to us we made numerous attempts to purify arsenical hydrochloric acid by making use of the principle just stated, but without success. It was found impossible to remove arsenic by this means at the ordinary temperature.

We need not enter further into a description of the numerous preliminary experiments we carried out before finally adopting our present process. Briefly, the process consists in digesting a mixture of constant-boiling hydrochloric acid and methyl alcohol under diminished pressure in a flask furnished with a reflux condenser for some hours in presence of bright electrolytic copper free from arsenic, and then distilling the acid over similar copper. Digesting with methyl alcohol alone has been found to be capable of removing all but the last traces of arsenic, but the purification is rendered complete and the process considerably expedited by the conjoint use of metallic copper. It is our practice, before commencing the digestion, to add a trace of metallic zinc, and our experience has shown this to be an advantage.

The details of the process are as follows :

To 1,500 c.c. of commercial hydrochloric acid, slightly above 1·1 specific gravity, about 40 c.c. of redistilled commercial wood-spirit are added. The mixture is contained in a Wurtz flask of 2 litres capacity. About 5 to 10 grams of arsenic-free granulated zinc are then added. The flask is connected with the reflux condenser by an ordinary cork in which is fixed a glass rod supporting a coil of electrolytic copper foil, having a surface of about 120 square inches. The side tube of the Wurtz flask having been plugged, the condenser is connected with an exhaust-pump, and the boiling commenced. With acid containing from ½ to 1 grain per gallon, about three hours' gentle digestion is sufficient, the copper being withdrawn and cleaned at least once during this period. During the digestion a black, tarry, fuming liquid distils over, and the greater part of this is caught in a vessel intermediate between the condenser and the pump. It is also advisable to interpose a second somewhat larger vessel containing water to absorb any hydrogen chloride which passes off. This water should be changed as often as necessary.

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A SIMPLE ARRANGEMENT OF LENSES FOR READING THE GRADUATIONS OF CHEMICAL AND ASSAY BALANCES.

By G. T. Holloway, F.I.C.

(*Shown at the Meeting, December 6, 1905.*)

The usual telescopic or portable lens arrangements are, as shown in the figure, replaced by lenses cemented on the rising glass-front of the balance. Plano convex lenses cemented with seccotine on the inside of the glass are preferred, but bi convex lenses cemented at the edges in two or three places to small discs of cork, or other soft material cemented on the glass, may be used, as shown in the case of the upper lens in the accompanying figure.

A 3-inch lens for the pointer reading is a convenient size, but a 2-inch lens is
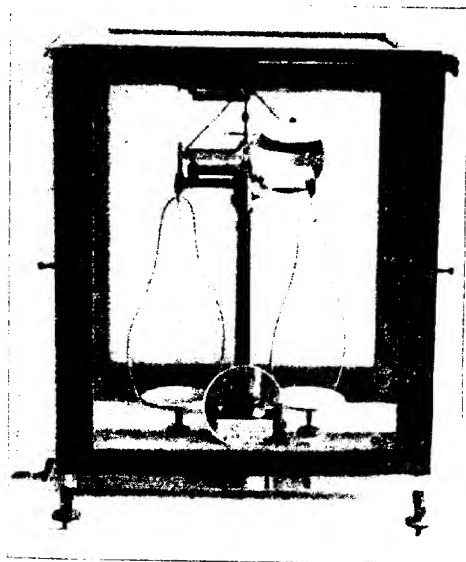
sufficient for reading the beam graduations. A slight movement of the head suffices to bring any part of the beam into the field.

The focal length of the lenses is of little importance, but they must not be powerful enough to produce distortion, or thick enough to prevent the rise and fall of the balance-front on which they are fixed. There is always sufficient space for any ordinary lens, and as the lenses are fixed inside, they remain clean and require no attention or adjustment. As the lenses are not required except when the rider is being used, they are out of the way while the balance-front is raised.

This arrangement is simple and cheap, and absolutely effective in saving strain to the eye, and may be applied with advantage even to a rough balance.

THE FACING OF RICE.

By Cecil H. Cribb, B.Sc. Lond., F.I.C., and P. A. Ellis Richards, F.I.C.

(Read at the Meeting, February 7, 1906.)

It has been a matter of more or less general knowledge for some years that rice is faced, *i.e.*, polished, with the aid of some extraneous substances, but we are not aware of any references to the subject beyond a note in the ANALYST (vol. ii., p. 152) on "waxed rice," a statement in the *British Food Journal* (1900, p. 46) that rice is finished with the aid of oil, paraffin oil being sometimes employed, and a paper by Matthes and Müller (*Zeit. öffentl. Chem.*, 1905), abstracted in the ANALYST (vol. xxx., p. 206). These authors mention the use of "talc" as a coating material for various cereals, including rice.

It was formerly the custom in some retail businesses, and may be so now, to polish the rice by shaking in a bag of sheepskin or other suitable material, the process being known as "trouncing." With the advent of machinery this simple method is no doubt a thing of the past ; but most of the earlier recorded analyses plainly show that, whatever the process employed, it did not as a rule involve the addition of any appreciable amount of *mineral* matter.

The following figures for the total ash of rice are given by the authors named :

	Total Ash.
Boussingault	0·5 per cent.
Fresenius	0·52 ,,
Polson	0·9 ,,
Poggiale	0·32 ,,
Cooley's " Encyclopædia "	0·5 ,,
Jago (" Chemistry of Wheat Flour," p. 233)	0·28 ,,
Bell (" Analysis and Adulteration of Foods," p. 86)	0·28 ,,
Wynter Blyth (" Foods : Composition and Analysis," p. 214) ...	0·45 ,,
Leffmann and Beam (" Food Analysis," p 101)	0·3 to 0·6 per cent.
Leach (" Food Inspection and Analysis," p. 213) :	
Unhulled	4·09 per cent.
Unpolished	1·15 ,,
Polished	0·46 ,,

Hassall, in a complete analysis of the ash, gives the silica as 3·35 and Leach as 6·14 per cent. of the total ash.

We have recently had occasion to examine a number of samples submitted to us under the provisions of the Sale of Food and Drugs Acts, and the very high proportion of ash in some of the samples, together with the presence of a substantial amount of mineral matter insoluble in hydrochloric acid, plainly indicated that some inorganic substance foreign to rice was present.

Table I. gives the total ash, together with the soluble ash and the ash insoluble in hydrochloric acid, in the samples referred to, and it will be seen at a glance that in every case but one the polished samples exhibit an increased total ash and a largely increased insoluble ash, as compared with the unpolished samples, thus clearly establishing the connection between the polishing and the excess of mineral matter

Also it may be mentioned that the sophisticated samples can be at once distinguished by the appearance of the ash as obtained in a muffle furnace. Genuine rice yields a fused glassy mass, whilst the ash of the polished samples exhibits a powdery appearance, and frequently retains, in skeleton form, the shape of the original granules. Further, it will be noticed that the variations in the total ash are almost entirely due to the substances insoluble in acid, the soluble ash being not only fairly constant in amount, but also almost always under 0·5 per cent.—i.e., within the limits of variation of the ash of natural unpolished rice.

TABLE I.

Samples of Unknown Origin.

	Price per lb.	Finish.	Total Ash.	Insoluble Ash.	Residual Ash.
1.	– –	Dull	0·29	trace	0·29
2.	1¼d.	,,	0·31	,,	0·31
3.	1¼d.	,,	0·32	,,	0·32
4.	3d.	,,	0·32	0·005	0·315
5.	----	,,	0·32	trace	0·32
6.	—	,,	0·32	0·01	0·31
7.	—	,,	0·33	0·01	0·32
8.	—	,,	0·37	0·035	0·335
9.	– – –	,,	0·38	0·03	0·35
10.	– – –	,,	0·42	0·02	0·40
11.	----	,,	0·57	0·02	0·55
12.	2d.	Polished	0·52	0·18	0·34
13.	---	,,	0·64	0·25	0·39
14.	----	,,	0·70	0·30	0·40
15.	2d.	,,	0·80	0·40	0·40
16.	1d.	,,	0·83	0·41	0·42
17.	2d.	,,	0·83	0·40	0·43
18.	1d.	,,	0·85	0·44	0·41
19.	--	,,	0·85	0·39	0·46
20.	2d.	,,	1·00	0·48	0·52
21.	2d.	,,	1·02	0·53	0·49
22.	1½d.	,,	1·07	0·71	0·36
23.	3d.	,,	1·07	0·66	0·41
24.	2½d.	,,	1·50	1·10	0·40
25.	1½d.	,,	1·60	1·10	0·50
26.	2d.	,,	1·92	1·46	0·46
27.	2½d.	,,	2·00	1·55	0·45
28.	2d.	,,	2·22	1·65	0·57

On further examination it was found that by agitating the rice with water and pouring off the turbid liquid, after the grains had settled to the bottom, and repeating the operation two or three times, the fine particles thus removed from the surface contained practically the whole of the insoluble ash, while the residual grains had the ash of genuine unpolished samples.

TABLE II.

	Insoluble Ash.	Ash of Powder removed by Levigation.
No. 25	1·10	1·05
Patna	0·73	0·68
No. 12	0·18	0·25
No. 26	1·46	1·52

More detailed analyses of the mineral matter in the samples will be found in Table V.

It appears that, while the ash of the unpolished rice contains only a trace of insoluble matter, and from 9 to 11 per cent. of magnesia (MgO) in a soluble form, in the polished rice the insoluble portion almost invariably forms at least 40 per cent. of the total ash, and consists mainly of magnesia and silica.

Although the substance used in the polishing process apparently adds comparatively little to the amount of soluble ash, nevertheless, the latter invariably contains an increased amount of magnesium, the result, no doubt, of the partial decomposition of the silicate by fusion with the alkaline salts of the soluble ash, as the following figures show :

TABLE III.

Rice.				Percentage of MgO in portion of Ash Soluble in HCl.
Carolina, unpolished	...	...	...	11·3 per cent.
„ polished	...	...	...	24·5 „
Patna, polished ...	...	...	...	23·5 „
Java, polished (A)	...	...	...	20·2 „
„ „ (B)	...	...	...	21·2 „

It may be taken for granted, therefore, that a compound of magnesia and silica is largely, though not universally employed in the polishing process. To get further information we have examined a number of samples of known origin and of every price and quality, very kindly supplied to us by some of the largest wholesale and retail houses in the trade, and the analyses of these are set forth in Table IV., p. 43.

The conclusions already arrived at are fully borne out by the foregoing figures, for with the exception of the samples described as "oil polished," all the polished samples contain excess of mineral matter, showing itself almost exclusively in the insoluble ash.

The absolute identification of the foreign substance is difficult, if not impossible. The powder washed off from the outside of the grains, when examined under the microscope, appears as transparent angular particles of irregular outline, which exhibit no particular characteristics, although they have a general resemblance to mica and talc.

TABLE IV.

Samples of Known Origin.

Rice.	Price.	Finish.	Total Ash.	Insoluble Ash.	Residual Ash.
Carolina	6d.	Dull	0·22	0·01	0·21
,,	4½d.	,,	0·29	0·02	0·27
,,	4d.	Polished	0·68	0·44	0·24
,,	4d.	,,	0·86	0·41	0·45
Patna :					
Foreign cleaned	3d. to 4d.	,,	0·71	0·30	0·41
,,	2½d.	,,	1·07	0·70	0·37
,,	2½d.	,,	1·14	0·73	0·41
Broken, London milled	2½d.	,,	0·90	0·50	0·40
,, ,, ,,	2½d.	Slightly polished	0·80	0·42	0·38
English cleaned	3d. to 4d.	,, ,,	0·87	0·47	0·40
,, ,,	3d.	,, ,,	0·92	0·56	0·36
,, ,,	3d.	,, ,,	1·08	0·78	0·30
Japan	3d.	Dull	0·22	0·001	0·219
Siam, Dutch cleaned		,,	0·40	0·03	0·37
Bassein :					
German cleaned	2d.	Polished	0·77	0·35	0·42
,, ,,	2d.	Polished (contains damaged grains)	1·10	0·60	0·50
Java :					
Natural cleaned	2½d.	Dull	0·33	0·015	0·315
Foreign cleaned	—	Polished	0·78	0·34	0·44
Indigo treated ...	1d.	,,	0·82	0·44	0·38
,, ,,	2d.	,,	1·26	0·90	0·36
English cleaned	2½d.	,,	0·71	0·31	0·40
,, ,,	2½d.	,,	0·74	0·43	0·31
,, ,,	2½d.	,,	0·99	0·71	0·28
,, ,,	2½d.	,,	1·14	0·73	0·41
Dutch cleaned ...	3d.	,,	0·40	0·07	0·33
,, ,,	3d.	,,	0·51	0·01	0·50
,, ,,	3d.	,,	0·54	0·25	0·29
,, ,,	3d.	,,	0·73	0·35	0·38
,, ,,	3d.	,,	0·99	0·49	0·50
Burma	1½d.	Dull	0·30	trace	
Rangoon :					
Rice with hull ...		Brown	2·62	1·42[1]	1·20
Rice de-hulled in the laboratory	—	Very dull	1·32	0·13[1]	1·19
Oil-dressed, in Holland	—	Slightly polished	0·30	0·01	0·29
Broken, London milled	—	Dull	0·52	0·17	0·37
Antwerp milled	—	Polished	1·15	0·82	0·35

* Probably polished by oil or some other process.
† Practically all silica.

Even the wholesale dealers appear to have no certain knowledge of the *modus operandi* of the polishing process, which seems to be a carefully-guarded trade secret, and no doubt differs slightly in different countries as regards both the method and the nature of the added substances. Steatite, French chalk, powdered talc, and mica are amongst the substances hinted at. We were informed that two of the Java samples had been treated with indigo in order to improve the colour, but we have so far been unable to verify the statement. The following table shows the composition of these, together with that of the insoluble matter actually found in the samples examined by ourselves:

TABLE V.

Polished Rice.				Percentage Composition of Silicious Matter.		
				SiO_2.	MgO.	$Fe_2O_3 + Al_2O_3$.
Carolina	...	...	..	61	22	present*
Patna	...	...	...	56	22	5·8
Java ...	...	...	...	58	24	present*
A. Unknown origin			...	62	22	,,
B.	,,	,, ...	...	62	25	6·1
C.	,,	,, ...	...	62	25	present*
D.	,,	,, ...	...	58	28	7·01
E.	,,	,, ...	...	61	20	9·00
French chalk		...	...	61	29	4·02
Talc ...	...	...	...	57	30	3·6
Steatite	...	...	...	62	33	3 to 4

Assuming that one or other of these substances is used, the difficult question which always confronts the Public Analyst in such matters at once arises—Is this method of treating rice to be regarded as adulteration?

On the one hand, it must be admitted that it is absolutely unnecessary, inasmuch as there are other modes of polishing which are not open to the same objection; and, moreover, there is no reason whatever, apart from the whims of certain purchasers, why the grains should not be left with their natural surface, as, indeed, is the practice of some of the chief rice-eating nations, notably Japan.

The proportion of foreign matter present in some of the samples is quite sufficient to constitute a fraud, inappreciable, perhaps, by the individual purchaser, but ample to give to one unscrupulous vendor an unfair advantage over his more honest rivals.

Further, on the medical aspect of the case, it has been suggested to us that there is the possibility that even very small quantities of an insoluble mineral substance may be injurious to health, not, of course, owing to any chemical action, but merely by the mechanical irritation it might set up, and because of the possible formation of fæcal concretions.

* Quantity not estimated.

On the other side, it has been urged that the proportion of foreign matter is at the worst small and at the best negligble; that the amount of irritation likely to be set up must be extremely slight, and would be quite as likely to be beneficial as otherwise by the promotion of peristalsis. As the alleged adulterant is more expensive than the rice itself, there could be no possible temptation to the manufacturer to adopt the process for the purpose of fraud, and in addition to this, it might also be urged that the foreign matter generally is, and always might be, largely removed during cooking. We understand this is the custom of native cooks in India, by whom the rice is always soaked and washed before use.

Whatever may be the opinion in regard to the legal aspect of the question, it is somewhat startling to reflect that an article of diet of such common and widespread use, hitherto accepted as one of the purest forms of vegetable food, should so frequently contain a substance of a foreign nature.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

The "Aldehyde" Value of Milk. R. Steinegger. (*Zeit. Unters. Nahr. Genussm.*, 1905, x., 659-671.) The addition of formaldehyde to milk causes an increase in the acidity of the latter, apart from that due to the acidity of the formaldehyde solution itself. The acidity increases with the quantity of formaldehyde added until it reaches a maximum with the addition of 1·8 per cent., or about 5 per cent. of the ordinary 40 per cent. formalin solution. The difference between the original acidity of the milk (expressed in Soxhlet Henkel degrees) and the acidity of the same after the addition of 5 or 6 c.c. of formalin is termed by the author the "aldehyde" value of the sample. This value for normal milks varies between 5·8 and 8·5. For the milk from single cows the value remains practically constant. In the case of colostrum the value rises as high as 17·3, but decreases as the milk becomes normal. The increase is observed with boiled milk, showing that the phenomenon is not due to the action of an oxidizing ferment. As the aldehyde value varies with the amount of casein and other proteids in the milk, the increase of acidity is undoubtedly caused by the chemical reaction between the formaldehyde and these proteids. The determination of the aldehyde value is proposed as a means of detecting the presence of added water in milk, as this form of adulteration decreases the percentage of proteids in the milk, and, consequently, the aldehyde value. Abstraction of fat does not influence the value. W. P. S.

The Quantity of Water in Canadian "Domestic" Butter. A. McGill. (*Canadian Inland Revenue Department*, Bull. 107, 1-12.)—By domestic butter is meant butter as found in the retail market, and intended for home consumption.

Of 180 samples of this class of butter examined, only 1 contained an amount of water in excess of 16 per cent. Eight of the samples contained from 14 to 16 per cent., and in 111 samples the water was below 10 per cent. One of the samples contained borate preservative.   W. P. S.

Detection of Phytosterol in Lard in the Presence of Small Quantities of Paraffin, and the Determination of Small Amounts of Paraffin in Lard.

E. Polenske. (*Arbeit. Kaiserl. Gesundheitsamte*, 1905, vol. 22, pp. 576-583.)—The sensitiveness of the phytosterol acetate test (ANALYST, 1902, xxvii., 94) is sometimes vitiated by the presence of traces of paraffin in the fat under examination. The paraffin becomes more and more concentrated as the acetate is recrystallized, until at last the melting-point obtained falls to that of the paraffin — that is, about 53° C. By taking advantage of the slight solubility of phytosterol in petroleum spirit, it is possible to remove the paraffin. The unsaponifiable residue obtained from 100 grams of fat in the usual manner is placed in a cylinder of about 8-c.c. capacity, and treated with 1 c.c. of petroleum spirit (boiling-point below 50° C.). After stirring up the residue with a glass rod, the cylinder is stoppered and placed aside for about twenty minutes. The whole is then poured on to a small pellet of cotton-wool placed in the stem of a funnel, and the residue and filter washed five times with petroleum spirit, using 0·5 c.c. of the latter each time. The residue of phytosterol is finally dissolved off the cotton-wool with a little ether, evaporated, and acetylated. Besides removing the paraffin, the above process concentrates the phytosterol in the residue, as cholesterol is considerably more soluble in petroleum spirit.

For the determination of small quantities of paraffin in fats the crude, un-saponifiable residue from 100 grams of the fat is heated in a strong glass tube with 5 c.c. of concentrated sulphuric acid to a temperature of 105° C. for one hour (a mixture of 40 parts of glycerol and 60 parts of water boils at 104 to 105° C.). After cooling, the contents of the tube are shaken out three times with petroleum spirit, using 10 c.c. each time, and continuing the shaking for one minute. The extracts are united, washed a few times with a little water, the petroleum spirit is evaporated, and the residue weighed after being dried at 100° C. Should only traces of paraffin be present it is advisable to subject the residue to a second treatment with sulphuric acid.   W. P. S.

The Determination of Tannin in Wine.

L. Kràmszky. (*Zeit. anal. Chem.*, 1905, vol. 44, pp. 756-765.)—It is shown that the method of Neubauer and Löwenthal gives not only the amount of tannin, but the sum of the tannin and colouring matters. Barth's colorimetric method has the same drawback, and is also not generally applicable. An ammoniacal solution of zinc sulphate (or of nickel sulphate) yields quantitative results with solutions of pure tannin, which agree well with those obtained by the Neubauer-Löwenthal method, and at the same time does not pre-cipitate the colouring matter of wine. · The reagent is prepared by dissolving about 25 grams of pure zinc sulphate in water, adding ammonia until the precipitate first formed redissolves, then an additional 300 c.c. of ammonia, and making

up the liquid to a litre. For the determination of the tannin 50 c.c. of a red wine or 100 c.c. of a white wine are rendered alkaline with ammonium hydroxide and heated, no notice being taken of any precipitate that may be formed. The liquid is then treated with 20 c.c. of the reagent and stirred until the zinc tannate separates, after which 300 c.c. of hot water are added, and the whole allowed to stand. The precipitate is repeatedly washed by decantation with hot, slightly ammoniacal water, and finally brought on to the filter (preferably a Gooch's crucible containing asbestos), dried at 100 to 130 C., and weighed. It is then oxidized by means of a few drops of strong nitric acid, and ignited after evaporation of the acid. The difference between the two weights gives the amount of tannin. The author gives a series of results thus obtained with solutions of pure tannin and with wines, including some to which had been added known quantities of tannin. Comparative determinations were made by the method of Neubauer and Lowenthal, the difference between the results in the case of red wines ranging from 0·02 to 0·08 gram. According to Neubauer, a deduction of 0·03 to 0·04 gram must be made for the colouring matters in dark-red wines when the permanganate method is used. As regards the question of gallic acid, the author considers that it is probably only present in traces in sound red wines, but that unsound wines may possibly contain considerably more. Experiments to determine the influence of gallic acid on the determination of the tannin by the zinc method have given the following results: (1) Gallic acid is not precipitated by ammoniacal zinc sulphate solution. (2) Wines to which a known quantity of gallic acid has been added give, on analysis by the method of Neubauer and Lowenthal, a higher value than corresponds to the sum of the tannin, colouring matter, and added gallic acid. (3) In certain cases the presence of gallic acid prevents the precipitation of part of the tannin by ammoniacal zinc sulphate solution. C. A. M.

A Honey Substitute. G. Reiss. *Arbeit. Kaiserl. Gesundheitsamte*, 1905, vol. 22, pp. 666-668.)—Under the name "Fruktin" an article has recently been placed on sale as a honey substitute. It consists of cane-sugar and a small quantity of tartaric acid, a little caramel being also present. According to the directions given with each packet of the article, 500 grams of the latter are heated to boiling with 150 grams of water, and the mixture then kept in a warm place for half an hour in order to obtain a honey-like product. The author has himself prepared artificial honey by treating "Fruktin" in this way, and from it obtained the following analytical data: Specific gravity of a solution of 1 part in 2 parts of water, 1·11; invert sugar, 53·39 per cent.; cane-sugar, 41·63 per cent.; ash, 0·024 per cent.; polarization of a 10 per cent. solution observed in a 200-mm. tube, +4°37'; after inversion, −2°44'. The proportion of cane-sugar is, as will be seen from the above figures, about four times greater than is found in natural honey, whilst the percentage of ash is much lower. At the same time, a mixture of 1 part of "Fruktin" honey with 3 parts of pure honey would contain about 10 per cent. of cane-sugar, and such mixtures would only differ from natural honey in their low percentage of ash and in the presence of tartaric acid in them. W. P. S.

Valuation of Saffron.　A. Jonscher.　(*Zeit. öffentl. Chem.*, 1905, xi., 444-447.)—The stigma of saffron possesses a considerably higher aromatic or spice value than the pistil, as it contains more ethereal oil and crocin. The stigma is also superior to the pistil as regards colouring power. An approximate method for determining the value of a sample of saffron consists in boiling 0·1 gram of the air-dried sample with 10 c.c. of 50 per cent. alcohol, at once cooling the mixture, and then allowing it to stand for one hour. The solution is then filtered, and 5 c.c. of the filtrate diluted to 100 c.c. with water. The coloration is then compared with that produced by a good specimen of saffron under similar treatment.　　W. P. S.

Determination of Vanillin.　J. Hanus.　(*Zeit. Unters. Nahr. Genussm.*, 1905, vol. 10, pp. 585-591.) Vanillin is quantitatively precipitated from its aqueous solution by *m*-nitrobenzhydrazide. The presence of the ordinary adulterants of vanillin, such as acetanilide, benzoic acid, salicylic acid, and sugars, is without influence on the precipitation. For the determination of vanillin in vanilla the following method, based on the above-mentioned fact, is described : About 3 grams of the vanilla, in small pieces, are extracted for three hours with ether. The ethereal solution is evaporated at a temperature of 60° C., the residue is dissolved in a little ether and filtered into a small flask, the filter being washed with ether. The ether is again evaporated, the residue heated with 50 c.c. of water for thirty minutes on the water-bath, and the emulsion so obtained precipitated with a solution of 0·2 gram of *m*-nitrobenzhydrazide in 10 c.c. of hot water. The flask and its contents are placed on the water-bath for thirty minutes, and then set aside for twenty-four hours. The mixture is now shaken out three times with petroleum spirit to remove fat, the extracts, after separation, being filtered in a Gooch's crucible, and the precipitate itself then rinsed on to the filter, washed first with water, then with petroleum spirit, dried at a temperature of 100 to 105 C., and weighed. The weight of the precipitate multiplied by the factor 0·4829 gives the amount of vanillin present.

The method is also applicable to the determination of vanillin in alcoholic extracts, but the alcohol must first be removed by evaporation at a low temperature.
　　　　　　　　　　　　　　　　　　　　　W. P. S.

The Determination of Iodine in Iodated Thymols. H. Cormimboeuf.
(*Ann. de Chim. anal.*, 1905, vol. 10, pp. 453-454.)—Iodated thymols (aristols) contain from 15 to 45 per cent. of iodine, according to the mode of manufacture. Most of the commercial products are chlor-iodo- rather than di-iodo thymols, and there is a risk of the whole of the halogen present being determined as iodine if the ordinary methods of Carius, etc., be used. The following method is recommended as giving only the iodine and requiring but little material : 0·5 gram of the sample is thoroughly mixed in a mortar with 3 grams of dry sodium carbonate, and the mixture heated gradually in a platinum or nickel crucible until nearly complete combustion of the organic matter, after which it is fused. The mass, when cold, is treated with hot water, the solution filtered from any particles of unburnt carbon, the filtrate mixed with half its volume of ammonium hydroxide, and the iodine precipitated

with silver nitrate in the usual way. The filtrate is acidified with nitric acid, a precipitate of silver chloride being obtained in the presence of chlorine. C. A. M.

Oil of False Savin. J. C. Umney and C. T. Bennett. (*Pharm. Journ.*, 1905, vol. 75, pp. 827-829.)—The oil of savin as distilled in this country, in Germany, and in the South of France, varies considerably. This is probably due to the fact that in the latter country the oil is distilled from false savin, *Juniperus Phœnicia* (the common Mediterranean species), whilst in the former the distillers use *Juniperus sabina*. The following results were obtained with three specimens of the oil :

			English. From *J. Sabina*.	German. From *J. Sabina*.	French. From *J. Phœnicia*.
Specific gravity	...	...	0·909	0·920	0·892
Optical rotation	.	...	+ 68°	+ 42°	+ 1 30′
Esters	...	...	47·6 per cent.	36·5 per cent.	9·3 per cent.
Total sabinol	...	...	52·1 ,,	48·2 ,,	17·1 ,,
Solubility in 90 per cent. alcohol	...	...	1 in 1	1 in 1	1 in 5
Portion distilling :					
Below 155° C.		...	nil.	nil.	18 per cent.
,, 165° C.	...	...	nil.	nil.	64 ,,
,, 175° C.	...	...	14 per cent.	nil.	68 ,,
,, 180° C.	...	...	23 ,,	4 per cent.	80 ,,
,, 200° C.	...	...	48 ,,	29 ,,	82 ,,
,, 220° C.	...	...	62 ,,	49 ,,	84 ,,
,, 230° C.	...	...	80 ,,	60 ,,	86 ,,

The oil from *J. Phœnicia* contains over 75 per cent. of pinene, the hydrochloride of which melts at 125° C., and the nitrosochloride, after one recrystallization, at 107 C. A sesquiterpene, cadenine, is also present in the oil. W. P. S.

Examination and Assay of Aloes. L. v. Itallie. (*Pharm. Weekblad*, xlii., 553; through *Pharm. Journ.*, 1905, vol. 75, p. 554.) The author considers that Tschirch's method (ANALYST, 1905, xxx., 249) is open to objection, and modifies it as follows : Five grams of the powdered aloes are warmed with 5 c.c. of methyl alcohol until a homogeneous liquid is obtained ; 30 c.c. of chloroform are then added, the mixture is shaken for five minutes, and allowed to stand until clear. The solution is decanted, evaporated to dryness, and the residue again dissolved in methyl alcohol and precipitated. This treatment is repeated a third time. By the use of this method Cape aloes were found to contain from 18 to 43 per cent. of resin, and Curacao aloes from 11 to 21 per cent. Objection is also raised to Tschirsh's proposed colorimetric determination of aloin by Schouteten's reaction (green fluorescence with borax solution) on the ground that it is far too subjective, the author finding 100 per cent. of aloin in a sample of aloes. Determination of aloin by precipitation, as tri-bromo-aloin, succeeded with pure aloin, but indicated 71 per cent. of aloin in

Cape aloes and 72 per cent. in Curacao, which results the author considers to be much too high. W. P. S.

Analysis of Powdered Extract of Nux Vomica. W. H. Lenton. (*Pharm. Journ.*, 1905, vol. 75, p. 864.)—The following process is particularly applicable to the analysis of the powdered extract of nux vomica, and is similar to Bird's method (*Pharm. Journ.*, xi., 4, 574), dilute alcohol being used as a solvent for the powder, and a mixture of ether and chloroform for the actual extraction. Ten c.c. each of ether and chloroform are placed in a dry separating funnel, 2 grams of the powder are introduced, then 5 c.c. of 90 per cent. alcohol and 3 c.c. of concentrated solution of ammonia are added, and, finally, 5 c.c. of water. The whole is well shaken for about one minute, allowed to settle, and the ether-chloroform layer drawn off into another separating funnel, where it is shaken with 5 c.c. of 10 per cent. ammonium carbonate solution. After shaking the ether-chloroform once more with ammonium carbonate solution, the former is drawn off and placed aside. The alkaline mother-liquor is twice again shaken out with 20 c.c. of the ether-chloroform mixture, and the extract washed with the ammonium carbonate used for the first portion drawn off. The mixed ether-chloroform solutions are then treated as usual for the determination of strychnine. W. P. S.

ORGANIC ANALYSIS.

Studies on Formaldehyde in Aqueous Solution. F. Auerbach. (*Arbeit. Kaiserl. Gesundheitsamte*, 1905, vol. 22, pp. 1-46.)—The formaldehyde solutions employed in the experiments described were prepared by subliming tri-oxymethylene in an atmosphere of nitrogen, and collecting the vapours in water. For the determination of formaldehyde the sulphite method of Lumière and Seyewetz (ANALYST, 1904, xxix., 288) was found to be very useful, but for small quantities the iodine method was preferred. The results of determinations of the molecular weights of solutions containing varying amounts of formaldehyde lead the author to conclude that formaldehyde exists in aqueous solutions for the greater part in a hydrated or polymerized form. As the temperature is increased the simple molecule predominates. On distilling formaldehyde solutions of any strength whatsoever the distillate is always poorer and the residue richer in formaldehyde than the original solution. This fact should be taken into consideration in the detection and determination of formaldehyde. It is further shown that the boiling-point at normal pressure of formaldehyde solutions falls from $100°$ to $99°$ C. as the concentration increases. W. P. S.

Distinction between Phenol and Cresols. C. Arnold and G. Werner. (*Apoth. Zeit.*, xx., 925; through *Pharm. Journ.*, 1905, vol. 75, p. 837.)—The following reactions are suitable for the identification of phenol and cresols:

Phenol.—To 10 c.c. of the solution to be tested are added 10 c.c. each of potassium hydroxide solution and alcohol and 1 drop of aniline. After shaking the mixture, 5 drops of hydrogen peroxide and 10 drops of sodium hypochlorite are added

and the whole again shaken. Phenol gives a transient dirty red coloration, changing to yellow; o-, m-, and tricresol, a violet, changing at once to green; p. cresol, a violet, which at once disappears.

o-Cresol. With ferric chloride o. cresol gives a blue colour, rapidly changing to green; phenol, m. cresol, and tricresol, a violet; p. cresol, a blue colour.

m-Cresol. On warming with a little phthalic acid and 5 drops of sulphuric acid m-cresol gives a cherry-red, phenol and tricresol a dark red, o. cresol a cherry-red, p-cresol an orange colour. When diluted with water and rendered alkaline with sodium hydroxide phenol gives a magenta, o-cresol and tricresol a violet-red, m. cresol a bluish violet, and cresol a yellowish colour.

Cresol. A dilute ammoniacal solution of cresol when boiled and treated with bromine water gives no coloration. Phenol and o. cresol treated in this way give a blue colour, m. cresol and tricresol a bluish-green.

If a trace of potassium nitrate be added to a solution of a little of the substance in sulphuric acid, a dark-red colour is obtained in the case of cresol, all the others giving an emerald green coloration. When diluted with water and treated with an excess of ammonia, cresol gives a yellow colour, all the others a green. W. P. S.

On the Inflammability of Celluloid Articles (according to experiments made by Fr. Gervais, director of the Laboratory of the Ministry of Finance, St. Petersburg.) J. Bronn. (Zeits. angew. Chem., 1905, xviii., 1976.) It is shown that when heated to 100° C. (for instance, by contact with a steam-heater) articles made of celluloid decompose exothermically. Although the quantity of heat developed is not sufficient to set the celluloid itself on fire, it will cause the paper used for packing to smoulder, a slight draught of air being then sufficient to cause the whole mass to ignite. The temperature of ignition of celluloid appears to be fairly high, ranging from 355° to 457 C. in the case of four articles examined, that of pyroxylin being only 130° C. White celluloid (imitation ivory) is more difficult to ignite than the other kinds. Celluloid articles may now only be sent to Russia when packed in wooden or metal cases. A. G. L.

The Detection of "Blown" Fatty Oils in Mixtures with Mineral Oil. J. Marcusson. (Chem. Rev. Fett-u. Harz. Ind., 1905, xii., 290-293.) "Blown" rape and cotton-seed oils are stated to be the two preparations of this kind most used in lubricating mixtures. Their presence cannot be detected by determination of the iodine value or molecular equivalent of the fatty acids. "Blown" cotton-seed oil does not give Halphen's or Millian's reactions, though it gives the brown coloration with nitric acid. The latter reaction, however, is also given by "blown" rape oil. The author relies upon the following tests to distinguish between the two "blown" oils: (1) The odour of the mixture and of the fatty acids, recalling that of the unblown oils. (2) The consistency of the fatty acids oily in the case of "blown" rape oil, semi-solid in that of "blown" cotton-seed oil. (3) The behaviour of the respective lead salts towards ether. Thus the amounts of fatty acids from the lead salts insoluble in ether ranged from 1·2 to 20·6 per cent. in the case of five "blown" rape oils, and 32·9 to 45·8 in the case of two cotton-seed oils. The difference was

more marked when the solubility of these fatty acids in petroleum spirit was compared, the rape oils yielding 0 to 8·7 per cent. and the cotton-seed oils 23·3 to 32·5 per cent. The fatty acids from the insoluble salts of the " blown " cotton-seed oil melted at 54° to 56° C., whilst those of the " blown " rape oil were oily or semi-solid. The following table gives results thus obtained, the amounts being calculated on the quantity of oil used in the preparation of the lead salts:

Kind of Oil.		Fatty Acids separated from Lead Salts insoluble in Ether.	
	Total Fatty Acids.	Fatty Acids soluble in Petroleum Spirit.	Fatty Acids insoluble in Petroleum Spirit.
	Per Cent.	Per Cent.	Per Cent.
Commercial " blown " rape oil ...	1·2	1·2	0·0
Ditto	14·5	5·7	8·8
Rape oil " blown " in laboratory...	20·6	8·7	11·9
Commercial " blown " cotton-seed oil	32·9	23·3	9·6
Cotton-seed oil " blown " in laboratory	45·8	32 5	13·3

C. A. M.

On the Determination of Sulphur in Liquid Fuels (Petroleum, Oil, etc.). J. Matwin. (*Zeits. angew. Chem.*, 1905, xviii., 1766.)—The author recommends a modification of Drehschmidt's method in place of that of Goetzl (ANALYST, 1905, xxx., 376) for the determination of sulphur in liquid fuels, as much larger quantities (50 to 100 grams) may be used : The fuel is burnt in a small lamp provided with a wick, the products of combustion being led through a 5 per cent. solution of potassium hydroxide contained in three wash-bottles. The difference in weight of the lamp before and after the experiment gives the quantity of fuel burnt. No test analyses are given.   A. G. L.

Determination of Sulphur in Petroleum and Bituminous Minerals. F. C. Garrett and E. L. Lomax. (*Journ. Soc. Chem. Ind.*, 1905, xxiv., 1212.)— A convenient quantity (0·7 to 1·5 gram) of the substance is intimately mixed in a small crucible with 3 or 4 grams of a mixture of 4 parts of pure lime with 1 of anhydrous sodium carbonate, and the crucible completely filled with this mixture. A larger platinum crucible is placed over the small one (mouth downward), the whole inverted, and the space between the two crucibles filled with the lime-soda mixture. The apparatus is then placed in a muffle furnace heated to bright redness, the mouth of the crucible being covered with a thick pad of asbestos board, which prevents distillation from the inner crucible before the mixture in the outer crucible is heated, due to radiation from the roof of the muffle, and the pad may be removed as soon as a flame appears. The roasting should be continued for two hours, after which the mixture is brought into water, any sulphide oxidized by bromine, and

the solution acidified, filtered, and precipitated by barium chloride in the usual way, the solution being allowed to stand on the water-bath for twenty-four hours before filtration, if the amount of sulphur is small. (*Cf.* ANALYST, 1905, xxx., 418.)

W. H. S.

Estimation of Tannin as Strychnine Tannate. S. R. Trotman and J. E. Hackford. (*Journ. Soc. Chem. Ind.*, 1905, xxiv., 1096.)—The present absorption methods of determination are very unsatisfactory, even when the hide powder is replaced by collin, and the authors have investigated a large number of bodies with the object of obtaining a compound of tannin which could be readily precipitated and weighed. Metallic salts proved useless, precipitation being incomplete, and after experimenting with many organic bases, including phenylhydrazine and various primary and secondary amines, the alkaloids were tried, and strychnine, one molecule of which combines with one molecule of tannin, finally adopted, as it does not precipitate gallic acid, and its tannate is highly insoluble in water. Sufficient material is extracted with alcohol in a Soxhlet extractor to yield about 0·5 gram tannin, the solution evaporated to 50 c.c., transferred to a 100 c.c. flask, and made up to the mark with water, thus precipitating any resins and similar bodies. These are filtered off through a dry Gooch crucible, and the tannin estimated in the filtrate, 25 c.c. of which are placed in a 250 c.c. flask, diluted with water, the cooled strychnine solution (prepared by dissolving 0·25 gram strychnine in 50 c.c. alcohol, and mixing with an equal volume of water) added, and the solution made up to 250 c.c. This method of treatment is essential, as otherwise the precipitate is difficult to filter. The contents of the flask are now filtered through a weighed Gooch crucible of platinum or porcelain, having a diameter at the bottom of 1 to 2 inches, with a thin mat of asbestos over the bottom. After filtration the tannate is partly air-dried, and the dehydration completed in a vacuum oven heated to about 60. The soluble non-tannins are determined by evaporating 25 or 50 c.c. of the filtrate from the resinous matter. The amount of tannin found by the method is invariably less than that obtained by the use of hide powder or collin. W. H. S.

The Detection of Biliary Pigments in Urine. L. Grimbert. (*Journ. Pharm. Chim.*, 1905, xxii., 487-492.)—The following method combines the principles of the methods of Hammarsten and Salkowski, but it is claimed that it is more simple than either : Ten c.c. of the urine are shaken with 5 c.c. of a 10 per cent. solution of barium chloride, and the mixture subjected to centrifugal force. The precipitate, consisting of the sulphate, phosphate, and bilirubinate of barium, is mixed with 4 c.c. of 90 per cent. alcohol containing 5 per cent. of hydrochloric acid, and heated for about a minute on the water-bath, after which the tube is allowed to stand. If the supernatant liquid over the deposit is bluish green or dark green the presence of biliary pigments is indicated, whilst in their absence the liquid is colourless. If there is a slight brownish tint the hydrochloric acid may have been insufficient to oxidize the barium bilirubinate, and in that case, and that case only, 2 drops of hydrogen peroxide (10 vol. solution) are added and the tube again heated on the water-bath, after which the green colour will appear. If the brown tint continues

after the addition of the hydrogen peroxide the presence of certain altered products of biliary pigments is indicated. These are only met with in urines that have been allowed to stand for some time. In certain pathological urines the separation of the barium bilirubinate is promoted by the addition of a few drops of a 10 per cent. solution of sodium sulphate.   C. A. M.

Estimation of Naphthalene in Coal Gas. C. J. D. Gair. (*Journ. Soc. Chem. Ind.*, 1905, xxiv., 1279.) —Three methods are described, the first a slight modification of Colman and Smith's, in which a measured volume of gas is passed through three Woulff's bottles, each containing exactly 500 c.c. of $\frac{N}{20}$ picric acid, the contents of the bottles mixed together in a 20-ounce flask, and heated on the water-bath at 60° C. until the precipitated naphthalene and naphthalene picrate have entirely dissolved, the flask being closed with a cork through which a glass tube dips into a beaker containing a small quantity of picric acid from the Woulff's bottles. This is afterwards returned to the flask and its contents cooled, when naphthalene picrate crystallizes out, is dried *in vacuo* or in a warm room, and weighed, whence the naphthalene may be calculated ; or an aliquot part of the clear residual picric acid may be titrated with $\frac{N}{20}$ sodium hydroxide, using lacmoid as indicator, showing the amount of picric acid taken up by the naphthalene. This method, though devised for pure coal gas, is applicable to impure gas if the ammonia be first removed by passing the gas through oxalic acid before entering the picric acid solution.

The second method, due to Somerville, consists in passing a known quantity of the gas through three glass tubes, 7 inches long and 1 inch wide, fitted up as Woulff's bottles, and each containing 35 c.c. of 70 per cent. alcohol. The alcoholic solutions are then mixed in a flask, oxalic acid added if necessary, until the ammonia is neutralized, as shown by litmus-paper, and filtered, the filter-paper being thoroughly washed with dilute alcohol. About 500 c.c. of concentrated picric acid are then added, the liquid agitated, and allowed to stand for half an hour, when all the naphthalene picrate will have separated, and may be filtered, slowly dried, and weighed.

A third method, devised by the author, depends on the solubility of naphthalene in acetic acid. A known volume of gas, usually not exceeding 3 to 6 cubic feet, is passed through 350 c.c. of acetic acid (specific gravity 1·044), contained in two Woulff's bottles, a small Woulff's bottle with 150 c.c. of picric acid being placed after the acetic acid to catch any unabsorbed naphthalene. The contents of all three bottles are mixed in a flask, and 500 c.c. of concentrated picric acid solution added, when the naphthalene picrate separates out at once in large flocculent masses, which are easily filtered off, dried, and weighed.   W. H. S.

INORGANIC ANALYSIS.

The Determination of Bismuth, and its Separation from Copper, Cadmium, Mercury, and Silver. A. Staehler and W. Scharfenberg. (*Berichte*, 1905, xxxviii., 3862-3869.)—The method described is based upon the quantitative precipitation of bismuth by sodium phosphate, even in the presence

of hydrochloric acid. From 10 to 20 c.c. of the solution of the bismuth salt (0·1 to 0·2 gram of bismuth) are diluted to 300 or 400 c.c., and heated to boiling, any precipitate of basic salt being redissolved by the addition of the smallest possible quantity of nitric acid. The boiling liquid is treated with a boiling 10 per cent. solution of trisodium phosphate, the quantity required depending upon the amount of free acid present. In the presence of much hydrochloric acid a larger addition of sodium phosphate is necessary. If the solution has become alkaline, it must again be rendered acid by means of a little nitric acid. After boiling for some time the precipitate is allowed to subside, the supernatant liquid tested with sodium phosphate, and if the precipitation be complete, the precipitate is collected while hot in a Gooch's crucible, washed with hot 1 per cent. nitric acid containing a trace of ammonium nitrate, dried at 120° C., ignited for five or ten minutes over a Bunsen burner, and weighed as $BiPO_4$. The tabular results quoted agree within fractions of a mgm. with the theoretical amounts.

Separation of Bismuth and Copper.—The bismuth is precipitated as above described, whilst the copper is precipitated from the filtrate by means of hydrogen sulphide, and weighed as cuprous sulphide (Cu_2S). Electrolytic determination is unsatisfactory in the presence of hydrochloric acid.

Separation of Bismuth and Cadmium.—After separation of the bismuth as phosphate, the cadmium can be determined by electrolysis of the ammoniacal filtrate after the addition of potassium cyanide, provided hydrochloric acid be absent. In the presence of hydrochloric acid it is best to precipitate the cadmium as sulphide, which is then dissolved in dilute nitric acid, and the solution electrolyzed after the addition of potassium hydroxide and potassium cyanide.

Separation of Bismuth and Mercury.—The filtrate from the bismuth phosphate is treated with a large amount of hydrochloric acid, and then with ammonia in excess, any precipitate formed being redissolved in hydrochloric acid, and the solution again rendered alkaline with ammonia. The liquid is next heated to the boiling-point, and immediately treated with hydrogen sulphide. After five to ten minutes the mercury sulphide separates out uncontaminated with free sulphur. It is collected on a Gooch's filter, washed with hot water, alcohol, and ether, dried at 105° C., and weighed.

Separation of Bismuth and Silver.—The bismuth can obviously only be separated in the absence of hydrochloric acid. The silver in the filtrate from the phosphate can be determined by the usual methods.

Separation of Lead and Bismuth.—It is suggested that a method of separation may be based on the precipitation of the two metals as phosphates, and the removal of the lead by boiling the precipitate with nitric acid (1 per cent.). Lead is quantitatively precipitated from a neutral solution by means of sodium phosphate, but the precipitate consists of at least three different phosphates, which are converted, however, by long-continued boiling into the tertiary phosphate.

C. A. M.

On the Precipitation of Metallic Gold. P. E. Jameson. (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1144.)—By the following method metallic gold may be

precipitated in one or two minutes in a form resembling silver chloride. A stick of potassium nitrite weighing about 5 grams is placed in a solution of 1 gram of gold chloride in 30 c.c. of water, and 5 c.c. of concentrated sulphuric acid are at once added. As soon as the brisk reaction which takes place is over, another piece of potassium nitrite of the same size as the first is added, and the solution stirred until the reaction is over. The gold will then be found at the bottom of the clear liquid in the form of dark brown nodules, which, after drying, are more yellow than ignited cadmium oxide. A. G. L.

Estimation of Platinum. Nordenskjold. (*Chem. Zeit. Rep.*, 1905, xxix., 293.) - Platinum is usually estimated as the metal by precipitating with sodium formate or with zinc. The former method can be carried out by treating the platinum solution with 2 grams sodium formate and a little ammonium acetate, diluting to 200 c.c., warming until the evolution of carbon dioxide slackens, and then heating for twelve hours. The platinum is apt to pass through the filter-paper, but this can be prevented by adding a little nitric acid. The second method gives a granular precipitate of platinum. Magnesium is preferable to zinc. About 17 cm. of magnesium ribbon should be used per gram of platinum, and dilute solution used. Excess of magnesium is removed by hydrochloric acid ; any magnesium oxychloride is at the same time dissolved out. The two methods give concordant results. For iridium, ruthenium, and rhodium a slight modification is necessary, as these metals are sensibly attacked by acids in the precipitated form ; only sufficient excess of magnesium to form oxychloride is used, the residue is heated, whereby the metals mentioned are rendered insoluble in acids, and the oxychloride of magnesium dissolved out with acid.

To estimate platinum in a mixture of this group, the heated metal powder is digested with aqua regia, when platinum (and palladium) go into solution.

E. K. H.

Note on an Antimonial Pigment for Enamels. P. Rasenack. (*Arbeit. Kaiserl. Gesundheitsamte*, 1905, vol. 22, pp. 653, 654.)—The author finds that a substance sold under the name of "Leukonin" consists almost entirely of sodium metantimoniate, and that it is soluble to a considerable extent in water and in solutions of sodium chloride, sodium carbonate, tartaric acid, citric acid, etc., antimony in every case going into solution. The author suggests that enamels made with this substance may yield antimony to weak acid liquids. W. P. S.

The Use of Potassium Periodate in the Detection of Manganese, Cobalt, and Zinc. S. R. Benedict. (*Amer. Chem. Journ.*, 1905, vol. 34, pp. 581-585.) —On adding a solution of potassium periodate to a solution of a manganous salt a deep-red precipitate (or coloration with very dilute solutions) is immediately produced. This precipitate is soluble in hydrochloric acid, and is converted by sodium peroxide into a black hydrated manganese dioxide. As a reagent, a $\frac{N}{16}$ solution of the potassium salt is capable of detecting 1 part of manganous chloride in 10,000, the test being more sensitive in a warm ammoniacal solution than in a neutral warm

solution. Zinc does not interfere with the reaction. Solutions of pure zinc salts yield a white periodate, but the presence of ammonium chloride and ammonium hydroxide prevent the formation of this, unless there is a very large amount of zinc. On boiling the filtrate from the precipitated manganese the zinc is precipitated. Conversely, a solution of manganese chloride may be used for the detection of periodate in the presence of iodate, iodide, etc. Iodates give no coloration with manganese in the presence of ammonium chloride and hydroxide.

Solutions of pure nickel salts react with potassium periodate to give a light-green precipitate, which becomes slightly grey on boiling, whilst cobalt salts yield a dark-brown precipitate, which becomes greenish on adding an excess of the reagent, and dissolves, forming a greenish-black solution on heating. If cobalt and nickel are present together, the precipitate will become more or less olive green on boiling, and the test is capable of detecting as little as 0·1 per cent. of the former. It is advisable, however, to make a comparative test with a solution of a pure nickel salt of the same strength. If the precipitate turns black, either in the cold or on boiling, traces of manganese are present. C. A. M.

Separation of Iron and Zinc by Means of Ammonia. W. Funk. (*Zeits. angew. Chem.*, 1905, xviii., 1657.) In the separation of iron and zinc by means of ammonia, the author shows that good results can be obtained if a large excess of ammonia is used in the presence of much ammonium chloride, the precipitate being washed with a 5 per cent. solution of ammonium chloride, and the precipitation being carried out twice. Practically the whole of the zinc is then found in the two filtrates. A. G. L.

Estimation of Metallic Iron in Presence of Ferrous and Ferric Oxides. B. Neumann. (*Chem. Zeit. Rep.*, 1905, xxix., 310.) Metallic iron can only be directly estimated in presence of ferrous oxide when no ferric oxide is present, otherwise the latter is reduced to ferrous oxide, using up hydrogen. The author therefore proposes the following indirect method : the substance is very finely powdered, and if only the content of metal is required, this is simply extracted with a magnet. In other cases the finely-divided substance is warmed with a measured quantity of a standard copper sulphate solution, and the precipitated copper directly estimated or, better, calculated from a determination of the copper left in the solution. This gives the metallic iron. Next the hydrogen given off on treatment with dilute sulphuric acid is measured. This represents only part of the hydrogen, some being used in reducing ferric oxide to ferrous oxide. The solution is then titrated with standard permanganate, which gives the original ferrous oxide dissolved and the reduced oxide. From these figures the original content of ferrous oxide can be calculated. The total iron is then estimated in the usual manner, and the ferric oxide obtained by difference. E. K. H.

Determination of Zinc in Zinc Aluminium Alloys. R. Seligman and F. J. Willott. (*Journ. Soc. Chem. Ind.*, 1905, xxiv., 1278.)—A rapid method for the approximate determination of zinc (within 0·2 per cent. of the gravimetric result)

consists in dissolving the alloy in caustic soda, precipitating the zinc as sulphide, redissolving in hydrochloric acid, and titrating the zinc with potassium ferrocyanide. Half a gram of the drilled alloy is dissolved in a 400 c.c. beaker in 25 c.c. of a 25 per cent. caustic soda solution, the liquid warmed till rapid evolution of gas takes place, and allowed to stand until solution is complete—usually five to ten minutes. The solution is then diluted to 300 c.c. with boiling water; any undissolved iron, copper, lead, tin, or nickel allowed to settle, and the clear liquid poured off, the residue being washed twice by decantation. This residue generally contains a small amount of zinc, which is removed by dissolving in a few drops of concentrated hydrochloric acid, diluting to 20 c.c., neutralizing with caustic soda, and adding 2 c.c. of the latter solution in excess. After warming the precipitated hydroxides are filtered off and washed, and the filtrate added to the main bulk of the zinc and aluminium solution. The zinc is now precipitated by sulphuretted hydrogen, which is passed till a skin forms at the point where the bubbles of gas burst, the precipitate allowed to settle, the clear liquid decanted, and the precipitate thrown upon a filter, whence it is dissolved in 8 c.c. hydrochloric acid, washed into the beaker used for precipitation, and diluted to 250 c.c. with boiling water. The presence of a small amount of alumina in the zinc is harmless, so that it is unnecessary to wash the precipitated sulphide. Five grams of ammonium chloride are then added, and the zinc titrated with a solution containing 22 grams of potassium ferrocyanide per litre, using uranium nitrate or acetate or ammonium molybdate as indicator. For the spot-tests a slab of paraffin wax or a porcelain plate covered with a thin coat of wax is recommended.   W. H. S.

The Determination of Barium as Chromate, and its Separation from Strontium and Calcium. A. Skrabal and L. Neustadtl. (*Zeit. anal. Chem.*, 1905, vol. 44, pp. 742-755.) The authors from a study of the different methods find that good results are obtained by precipitating the barium by means of ammonium bichromate from a neutral or slightly acid solution in the presence of ammonium acetate. The precipitation may be made from a hot or cold solution, but the filtration and washing of the precipitate must be done in the cold. Barium can be separated from calcium with approximately correct results by means of a single precipitation with ammonium bichromate from a cold, very dilute acetic acid solution in the presence of ammonium acetate. Better results are obtained, however, by a double precipitation. It is impossible to effect a complete separation of barium from strontium by means of a single precipitation with ammonium bichromate. The following combined method is recommended for the separation of barium from calcium and strontium: The neutral or slightly acid solution of the salts (about 0·135 gram of the respective oxides) is mixed with ammonium acetate in excess (10 c.c. of a solution containing 300 grams per litre), brought to the boiling-point, and treated with ammonium bichromate solution (5 c.c. of a solution containing 100 grams per litre), added drop by drop, with continual shaking. The precipitate is allowed to subside, and when cold washed by decantation with a dilute solution of ammonium acetate (20 c.c. of the above solution diluted to a litre) until the washings passing through the filter are colourless. The small amount of the precipitate that

has been retained by the filter is dissolved in warm dilute nitric acid, the solution and washings returned to the original beaker, and sufficient nitric acid added to dissolve the whole of the precipitate. The clear solution is now treated drop by drop with ammonium hydroxide until the first signs of a permanent turbidity appear, after which ammonium acetate is added (10 c.c. of the strong solution), and the liquid boiled and allowed to cool gradually. The precipitate is washed by decantation and on the filter with cold dilute ammonium acetate solution, then dried, ignited in a platinum crucible, and weighed. Strontium and calcium are then determined in the united filtrates in the usual manner. C. A. M.

The Determination of Titanium in Soil and the Ash of Plants. H. Pellet and C. Fribourg. (*Ann. de Chim. anal.*, 1905, vol. 10, p. 413-416.) I. *Direct Colorimetric Method.*—Half a gram of the dry earth, or 2.5 grams of ash, are introduced into a platinum crucible containing 15 grams of pure hydrofluoric acid and 1 c.c. of sulphuric acid, and evaporated to dryness. The residue is powdered, mixed with 5 grams of potassium bisulphate and fused, and the resulting product taken up with water containing 15 c.c. of sulphuric acid per 100 c.c., at a temperature not exceeding 60° C. The liquid is made up to 100 c.c. (there should be no insoluble residue), 1 to 10 c.c. taken and made up to 100 c.c. with distilled water, treated with 5 c.c. of hydrogen peroxide (12 volume solution), and compared colorimetrically with solutions of pure titanic acid containing 0.1 to 1.0 gram per litre.

II. *Gravimetric Methods.*—In the case of soils containing about 2 per cent. of titanic acid, 3 grams of the dried and finely-powdered sample are introduced little by little into a platinum crucible containing 30 grams of hydrofluoric acid, the mixture evaporated to dryness on the water bath, after the addition of 3 c.c. of sulphuric acid, and the residue powdered and fused with 15 grams of potassium bisulphate. After cooling, the mass is powdered and dissolved in 200 to 250 c.c. of water at a temperature of about 60° C., and the solution, when cold, made up to 300 c.c. and filtered: 250 c.c. of the liquid is next transferred to a 400 c.c. beaker, and 10 c.c. of the remainder titrated with a solution of potassium hydroxide, 10 c.c. of which neutralize 5 grams of potassium bisulphate. From the result can be calculated the amount of potassium hydroxide solution to be added to the 250 c.c., so as to leave 5 grams of potassium bisulphate still unneutralized. After this addition, the liquid is treated with 50 c.c. of a freshly-prepared solution of sulphurous acid (1.020 to 1.025 specific gravity) and boiled for two hours, in the course of which two fresh additions of 50 c.c. each of the sulphurous acid solution are made. It is then filtered, and the precipitate washed with boiling water and ignited, the residue being nearly pure titanic acid, with a little phosphoric acid. It is fused with pure potassium carbonate, the mass taken up with boiling water, and the insoluble portion washed with a 2 per cent. solution of potassium carbonate. The titanic acid remains behind in the form of an insoluble titanate, and the traces that pass into solution can be determined by a blank experiment with pure titanic acid. This titanate is ignited, fused with 1 gram of potassium bisulphate, and treated as above described, the residue of titanic acid being ignited and weighed.

In the case of soils containing less than 1 per cent. of titanic acid, 2 portions of 5 grams each of the finely-powdered and dry sample are ignited in separate platinum crucibles to destroy organic matter, and then fused with a mixture of 10 grams of sodium carbonate and 10 grams of potassium carbonate. The products of the fusion are taken up with very dilute hydrochloric acid, so as to form one solution, the silica separated by evaporating the liquid to dryness and igniting the residue, this being again taken up with dilute hydrochloric acid and the liquid filtered. The residual silica is treated with a mixture of hydrofluoric acid and sulphuric acid, which leaves a sulphated residue, whilst the filtrate is treated with ammonia, and the resulting precipitate separated from the filter and dried (the filter-paper being ignited alone). The united residue from the silica and ammonium precipitate is then fused with 15 to 20 grams of potassium bisulphate, and the titanic acid determined as described.

In the case of the ash of plants containing about 0·2 per cent. of titanic acid, 50 grams are treated with dilute hydrochloric acid, the silica separated, and the titanium determined in the filtrate.   C. A. M.

Rapid Method for the Valuation of Fluor-spar. A. W. Gregory. (*Chem. News*, 1905, vol. 92., pp. 184-185). -The following method may be found useful for the determination of calcium fluoride in fluor-spar when carbonates and silica are present in the mineral, all the determinations being carried out on the sample previously dried at 120° C. The carbon dioxide is determined by heating 2 grams of the sample to a red heat, until no further loss in weight takes place. Two grams of the sample are treated in a platinum basin with pure hydrofluoric acid, evaporated, ignited, and weighed. The calcium carbonate is thus converted into fluoride, and the loss in weight obtained is due to the silica present after allowance has been made for the quantity of carbonate previously found. (When the silica is present partly as silicate, this determination is not strictly accurate.) Another quantity of 2 grams of the sample are now heated in a platinum basin with concentrated sulphuric acid, hydrofluoric acid being first added if the amount of silica present be large. The excess of sulphuric acid is then driven off and the residue ignited and weighed. In this operation there will be an increase in weight, due to the conversion of calcium carbonate and fluoride into sulphate, and a loss of any silica present. The amounts of carbonate and silica being known, the fluoride may be calculated.
                                                                              W. P. S.

Electrolytic Calcium. Joseph H. Goodwin. (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1403.)—Metallic calcium can be easily and quickly prepared from calcium chloride by using the apparatus described. It consists essentially of a hollow cylinder of Acheson graphite, which is used as anode, the bottom being formed of a cooling copper coil, insulated from the graphite by asbestos. The cathode is a ¾-inch iron rod mounted on a screw arrangement, by which it can be raised or lowered. The calcium separated at first acts as cathode during the remainder of the operation, and, by gradually raising the iron cathode, sticks of metallic calcium are easily obtained. The reaction is started by filling the anode with cold calcium chloride, and

producing an arc between the cathode and anode; as the calcium chloride melts, the cathode is lowered into it until electrolysis takes place, the heat generated being sufficient to keep the salt fused. The temperature must be kept within rather narrow limits, otherwise the calcium separates in a spongy instead of a coherent form. As, with the heavy currents used, the asbestos does not completely insulate the copper coil from the anode, a cell is inserted between the copper and the graphite so as to cause a small current (0·01 ampère) to flow in the other direction; this device effectually prevents contamination of the calcium by copper. In six experiments, with voltage varying from 14 to 22, and ampérage from 105 to 185, a current efficiency of 21·5 to 41·9 per cent. was obtained, the average figures being: Volts, 17·7; ampères, 163·0; efficiency, 26·6 per cent. In six hours about 150 grams of calcium can be obtained. In one experiment the separated metal had the following composition: Ca, 98·00; Si, 0·03; Fe, 0·02; Al, 0·03; Mg, 0·11; Cl, 0·90; and O, by difference, 0·91 per cent. This sample had a conductivity of 3·43 microhms per c.c. at 0° C., the temperature coefficient being 0·00457, and a tensile strength of 8,710 lbs. per square inch, the elongation being 23·0 per cent. for 1 cm., 15 per cent. for 2 cm., 11·0 per cent. for 3 cm., and 6·6 per cent. for 5 cm. Calcium was found to be harder than sodium, lead, or tin, almost as hard as aluminium, but softer than zinc, cadmium, or magnesium. Its specific gravity was found to be 1·5446 at 29·2° C.

To clean the metal, after breaking off most of the calcium chloride, it is placed in 95 per cent. alcohol for some time, the loss owing to reaction with water and alcohol not being very great. The solid metal can be heated to a red-heat in air without igniting. It is not hardened by quenching in water. At 300 to 400° C. it is as soft as lead. When cold, the bright surface of the metal rapidly dulls in air, but when hot its surface may be polished, and will keep bright as long as the metal remains hot. By placing the hot metal in a bottle heated to 150° C., and closing the bottle while at this temperature, the surface may be preserved quite bright. A number of the cylinders obtained were fused together in a closed iron tube and quickly cooled, when a mass of large reddish-violet cubical crystals was obtained, having the following composition: Ca, 91·28; gangue, 0·03; SiO$_2$, 0·77; Fe$_2$O$_3$, 0·46; Al$_2$O$_3$, 0·77; Mg, 0·11; Cl, 1·28; C, trace; N, trace; O, by difference, 5·30. The specific gravity of the crystals was 1·5125 at 28·4° C.; they were quite soft, and could be hammered into sheets as thin as paper, often exploding with a slight flame under the impact of the hammer.   A. G. L.

Estimation of Percentage of Nitric Acid in the Concentrated Acid by the Specific Gravity. Veley and Manley. (Chem. Zeit. Rep., 1905, xxix., 1207.)—The authors publish some figures and details of their methods of purification, etc., in consequence of the divergence shown between the results published by Lunge and by Winteler.

The authors come to the conclusion that Winteler's acid was not sufficiently pure. They purified their acid as follows: The purest commercial acid was distilled, and the distillate was redistilled over silver and barium nitrates to remove sulphuric and hydrochloric acid. A current of ozonized oxygen was then passed

through, and finally the acid was fractionated *in vacuo* at the lowest possible temperature. In this way an acid was obtained containing 99·8 per cent. HNO_3 with only 1 part per million of nitrous acid, 4 per million of sulphuric acid, and 3 per million of halogen acids. This acid was further freed from water by a special apparatus (*Phil. Trans.*, 1890, A. 365), and an acid finally obtained which contained 99·97 per cent. HNO_3.

The authors used for titrating the various dilutions of this acid a sodium hydroxide solution prepared from sodium and steam, and a N-sulphuric acid solution standardized against sodium carbonate.

The following table shows the figures obtained by various observers :

Specific gravity :	1·485	1·490	1·495	1·500	1·505	1·510	1·515	1·520
Percentage according to								
1. Lunge and Rey ...	87·7	89·6	91·6	94·1	96·1	98·1	99·1	99·7
2. Veley and Manley ...	87·5	89·6	91·1	91·0	96·5	97·8	98·7	99·8
3. Ferguson ...	87·6	89·7	91·4	93·7				
4. Mean of first three series	87·6	89·6	91·4	93·9	96·1	97·9	98·9	99·8
5. Winteler ...	86·3	88·2	90·2	91·8	93·6	95·6	97·3	99·7
Difference between 4 and 5	1·3	1·4	1·2	2·1	2·8	2·3	1·6	—

For further comments on these figures, reference should be made to the original; but the authors express the view that the clearing up of the question lies with Winteler rather than with the other observers.   E. K. H.

Estimation of Percentage of Nitric Acid in the Concentrated Acid by the Specific Gravity. H. Pützer. (*Chem. Zeit. Rep.*, 1905, xxix.)—Compare paper by Veley and Manley, (see previous abstract). He adds his contribution to the figures already published. Great care was bestowed by the author on the purification of the acid. One hundred and fifty grams of this on evaporation in a platinum dish left a scarcely visible residue which was not weighable; the acid was quite free from nitrous acid (when diluted with water (5:1) and 1 drop of $\frac{1}{n}$ potassium permanganate added it remained pink for an hour), sulphuric acid, hydrochloric acid, and iodine.

The author having found the ordinary method of obtaining sodium carbonate from so-called chemically pure sodium bicarbonate unsatisfactory, he therefore prepared $Na_2CO_3.H_2O$ by boiling a solution of the bicarbonate and re-precipitating. This was then heated in a platinum dish by a burner whose flame-tip was about 5 cm. below the bottom of the dish. $\frac{1}{n}$ Na_2CO_3 was used, with methyl orange, very dilute, as indicator. The specific gravity was determined by a hydrometer showing the first three decimal places exactly, and the fourth by estimation.

The author's figures are :

Specific Gravity $\frac{17}{4}$ (Vac.)	Pc. HNO_3.	Specific Gravity $\frac{17}{4}$ (Vac.)	Pc. HNO_3.
1·4878	89·19	1·5018	95·51
1·4908	90·40	1·5033	96·13
1·4923	90·98	1·5043	96·59
1·4943	91·79	1·5058	97·21
1·4958	92·52	1·5073	97·76
1·4973	93·22	1·5103	98·62
1·4988	93·93	1·5128	99·20
1·4998	94·53	1·5163	99·75

By graphic interpolation these figures give results differing uniformly by 0·5 from those of Lunge and Rey.

The author considers that these differences are due to the fact that his acid was even purer than that used by Lunge and Rey, whilst Winteler's results may be rejected, as the acid used was, on his own showing, not pure.   E. K. H.

On the Determination of Sulphuric and Nitric Acids in "Nitrous Vitriol." G. Lunge and E. Berl. (Zeits. angew. Chem., 1905, xviii., 1684.) As the result of determinations made, partly on a synthetic, partly on a commercial acid, the authors recommend that nitro-sulphuric acid should be examined for (a) total acidity, (b) permanganate consumed, (c) total nitrogen by means of nitrometer. The nitric acid may then be calculated by subtracting (b) from (c), and the sulphuric acid by subtracting (c) from (a). Gravimetric determinations of sulphuric acid as barium sulphate tend to give high results; determinations of the nitric acid by the "nitron" method easily lead to low values. Evaporation of the nitric acid and titration of the residual sulphuric acid generally gives results slightly too low for the sulphuric acid, and consequently a little too high for the nitric acid.

    A. G. L.

Modification of W. Winkler's Method for the Determination of Oxygen in Waters. Hermann Noll. (Zeits. angew. Chem., 1905, xviii., 1767.) The author believes that with ordinary waters Winkler's method gives more exact results if the correction made by Winkler for the iodine consumed by the organic matter present is not made. When a correction must be made, as in the case of sewage effluents, he proceeds as follows: A mixture of 2 c.c. of 10 per cent. sodium hydroxide solution, 2 c.c. of 50 per cent. manganous chloride solution, and 30 c.c. of distilled water is shaken in a large flask until it becomes brown in colour; 50 c.c. of concentrated hydrochloric acid are then added, and the whole made up to 300 c.c. with distilled water. Of this solution, 20 c.c. are added to 100 c.c. of the water under examination, and also to 100 c.c. of distilled water. After five minutes 10 c.c. of a 5 per cent. potassium iodide solution are added to each, and the iodine liberated is determined with a solution of sodium thiosulphate, 1 c.c. of which corresponds to 0·1 c.c. of oxygen. The difference between the two values found gives the quantity of iodine taken up by the organic matter in the water, and may be applied as a correction to the results found by Winkler's method. Results obtained in this way on several waters agreed better with gasometric determinations of the oxygen in the waters than the values found using Winkler's method of correction.   A. G. L.

APPARATUS.

Alternating Motion for Stirrers. (Chem. Zeit., 1905, xxix., 1208.) Two stirring wheels are used, which rotate in opposite direction, and are so arranged that one of them is worked by the friction due to a projection on the main wheel during half a revolution of the latter, whilst the other is worked by a second projection on

the other half of the main wheel. The two paddles, therefore, work each through the time of a half revolution.

The apparatus is protected, and can be obtained from Franz Hagershoff, Leipzig.

E. K. H.

Note on the Incandescent Mantle as a Catalyst, and its Application to Gas Analysis. J. E. Mason and J. Wilson. (*Proc. Chem. Soc.*, 1905, vol. 21, p. 296.) Although less effective, the ordinary gas mantle may be used as a substitute for platinized asbestos in the preparation of formaldehyde from methyl alcohol vapour and air, and sulphur trioxide from sulphur dioxide and oxygen. Fragments of mantle in a hard glass or quartz tube may be employed in the place of palladium or palladium-asbestos for the determination of hydrogen and carbon monoxide by combustion with excess of air or oxygen. Methane and mixtures of methane and hydrogen may be determined similarly, the contraction being measured after combustion and subsequent treatment with potassium hydroxide solution. The results agree well with those obtained by the ordinary explosion methods. Good results may also be obtained by passing the gases mixed with oxygen over asbestos heated in a small quartz tube. Hydrogen, and less readily methane, may be determined by passing the gas mixed with oxygen through narrow tubes of heated Jena glass alone. W. P. S.

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INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Past List of the January Examinations.

Of fourteen candidates who entered for the Intermediate Examination, ten passed A. P. Davson, F. W. Foreman, W. Garsed, T. R. Hodgson, B.A. (Cantab.), T. J. Kirkland, A. Lathwood, B.Sc. (London), B. D. W. Luff, J. F. Reid, H. Stanley, B.Sc. (London), and F. Tattersfield. In the Final Examination for the Associateship (A.I.C.), of five examined in the branch of Mineral Chemistry, two passed: E. R. Bullock, Assoc.R.C.Sc. (London), and T. F. Cowie; of four in Metallurgical Chemistry, two passed: H. J. B. Rawlins, B.Sc. (London), and Thomas Stenhouse, B.Sc. (London), Assoc.R.C.Sc. (London), A.R.S.M.; of four in Organic Chemistry, three passed: W. P. Hayworth, F. H. G. Horsman, B.Sc. (London), and D. Spence, Ph.D. (Jena); and of twelve who entered in the branch of the Analysis of Food and Drugs and of Water. including an Examination in Therapeutics, Pharmacology, and Microscopy, the following nine passed: J. T. Cart, B.Sc. (London), C. G. Gates, B.Sc. (London), A. G. Holbcrow, Miss E. S. Hooper, B.Sc. (London), S. J. Lewis, B.Sc. (London), A. J. C. Lickorish, S. G. Liversedge, Miss E. A. Macadam, F. E. Thompson, Assoc.R.C.Sc. (London). The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A., F.I.C. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A., F.R.S., F.I.C.

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The annual meeting of the Society was held on Wednesday evening, February 7, in the Chemical Society's Rooms, Burlington House. The President, Mr. E. J. Bevan, occupied the chair.

The minutes of the previous meeting were read and confirmed.

Dr. L. T. Thorne and Mr. J. H. B. Jenkins were appointed scrutators of the ballot-papers for election of Officers and Council.

The Hon. Treasurer (Mr. E. W. Voelcker, A.R.S.M.) presented his annual report, with the accounts of the Society for 1905.

On the motion of Mr. Arthur R. Ling, seconded by Mr. John White, the report was unanimously adopted, and a vote of thanks accorded to the Hon. Treasurer for his services during the past year.

The Hon. Treasurer, having responded, proposed a vote of thanks, which was unanimously passed, to the auditors, Mr. W. P. Skertchly and Mr. Arthur R. Ling.

A vote of thanks to the Hon. Secretaries, Mr. Alfred C. Chapman and Mr. P. A. Ellis Richards, was proposed by Dr. Dyer, seconded by Dr. Schidrowitz, and unanimously passed.

Mr. Chapman acknowledged the vote of thanks.

A vote of thanks to the President and Council of the Chemical Society for their kindness in allowing the Society the use of their rooms at Burlington House during the past year was moved by the President, and unanimously agreed to.

The President delivered his annual Address.

Mr. Hehner proposed that a very hearty vote of thanks be accorded to the President for his Address, and that his permission be asked to publish the Address in the Analyst.

Mr. Kitto seconded the resolution, which was carried unanimously.

The President briefly responded.

The scrutators having reported to the President the result of their examination of the ballot-papers,

The President announced that the Officers and Council for 1906 had been elected as follows:

President.—E. J. Bevan.

Past-Presidents (limited by the Society's Constitution to ten in number). M. A. Adams, F.R.C.S.; A. Dupré, Ph.D., F.R.S.; Bernard Dyer, D.Sc.; Thomas Fairley;

The monthly ordinary meeting of the Society was held on Wednesday evening, February 7, in the Chemical Society's Rooms, Burlington House, immediately after the annual meeting. The President, Mr. E. J. Bevan, occupied the chair.

Certificates of proposal for election to membership in favour of Messrs. S. Dickson, J. Evans, F. Hughes, G. Patterson, and H. Thompson, were read for the second time; and certificates were read for the first time in favour of Messrs. George Craig, F.I.C., 95, Bath Street, Glasgow, analytical and consulting chemist; John B. Gall, F.I.C., A.C.G.I., Knoxland, Erith Road, Belvedere, works chemist to Messrs. Callender's Cable and Construction Company, Limited; H. Norman Hanson, Field Head, Brighouse, assistant to Mr. F. W. Richardson; Bernard W. Methley, 21, Clifton Mount, Rotherham, chemist to Messrs. Steel, Perch and Tozer, Sheffield; Frank Darby Ratcliff, 203, Ashted Row, Birmingham, chemist to Messrs. Holbrooks, Limited; and Frederick Robertson, 128, Wellington Street, Glasgow, analytical and consulting chemist.

Dr. H. W. Wiley was elected an honorary member; and Messrs. Geo. Clarke, Junr., C. A. Hill, B.Sc, and H. J. Horton, were elected members of the Society.

The following papers were read: "Note on Dutch Cheese," by Cecil H. Cribb, B.Sc.; "The Assay of Mercury Ores," by G. T. Holloway, A.R.C.Sc.; "The Purification of Zinc and Hydrochloric Acid," by L. T. Thorne, Ph.D., and E. H. Jeffers; and "The Facing of Rice," by Cecil H. Cribb, B.Sc., and P. A. Ellis Richards.

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THE ASSAY OF MERCURY ORES.

By GEORGE T. HOLLOWAY.

(Read at the Meeting, February 7, 1906.)

ALL the mercury of commerce is obtained by the roasting of cinnabar (HgS) in a current of air. The sulphur burns to the dioxide, and the liberated mercury, together with such native mercury as is frequently associated with the cinnabar, distils over and is collected in condensers and flues. Despite the enormous difficulty which is experienced in condensing the mercury and minimizing loss by leakage and flouring, the cheapness of the process and its comparative simplicity render it possible to treat

ores of extremely low value, and the bulk of the mercury now produced has been obtained from ores containing an average of between ¼ per cent. and 1 per cent. of the metal. It is true that ore as rich as 7 to 8 per cent. is worked at Almaden, in Spain, the oldest and richest mine in the world; but at Idria (Austro-Hungary), Nikitowka (South Russia), and Napa Consolidated Mines (California) respectively standing second, third, and fourth in order of production, the ore averages well under 1 per cent., as it does also in all other mines whose outputs are sufficiently large to count as factors in the world's production, which is stated to have amounted in 1904 to 3,581 tons of 2,240 pounds.

Cinnabar and native mercury usually occur impregnating or disseminated throughout limestones, dolomites, sandstones, etc. Copper and other ores frequently contain mercury, but not in quantity sufficient for extraction on the large scale. Bituminous matter commonly occurs in association with it, and in a few districts, as in Kweichow (China), antimony sulphide is met with, and seriously interferes with the extraction on account of the flouring of the mercury. The cinnabar and native metal, although frequently found in masses and occasionally in crystals, is practically all so mixed with the gangue and is so friable and, notwithstanding its great density, so easily lost when "dressed," that no dressing plant has been found capable of treating it profitably, and although hand-picking is occasionally practised, almost the whole of the ore is roasted exactly as it leaves the mine.

The old method of assay consisted in heating a mixture of the ore with iron filings or litharge or lime to redness in a glass tube closed at one end and bent down at the other, which latter dipped into water. A length of magnesite or sodium bicarbonate at the closed end of the tube permitted the generation of a stream of carbonic acid gas to drive the remaining mercury vapour out of the tube after the ore had been decomposed. The mercury was collected, dried, and weighed as metal.

This method is excellent for picked or rich material assaying, say, 20 per cent. or more, and, as stated later, is still probably the most accurate for such material, on account of the large amount of ore which can be taken for assay, but is absolutely useless for the ordinary ore, which probably accounts for 99 per cent. of the world's output. Wet processes are inapplicable to such ore. The well-known Eschka process (*Zeit. für Anal. Chem.*, vol. ii., p. 334), in which a small quantity of the ore was heated with iron filings in a small crucible, and the evaporated mercury was collected on a weighed disc of gold, was therefore introduced. The gold disc was cup-shaped, and was formed with a flange fitting on the crucible top. It contained cold water, which was occasionally renewed during the progress of the test. The mercury became condensed on the gold, which, after being weighed, only required to be heated gently to drive off the mercury ready for the next test.

As regards accuracy, Eschka's process leaves little to be desired, and the use of a strip of gold foil placed at the open end of a small ignition tube of about ⅛-inch bore, in which a mixture of iron filings and a mineral or salt containing mercury is heated, forms a most delicate test for mercury.

The presence of mercury to the extent of only $\frac{1}{100}$ of 1 per cent. may thus be proved, and accurate estimations may be made when the total mercury only amounts to $\frac{1}{16}$th per cent.

In 1898, R. E. Chism (*Engineering and Mining Journal*, October 22, 1898, p. 486) introduced a modification in which the gold cup was replaced by a piece of silver foil pressed into shape into the top of the crucible, and his results appear to have been perfectly satisfactory.

The modification about to be described differs from that of Eschka or Chism only in the construction and arrangement of the apparatus, and is shown in the accompanying drawing.
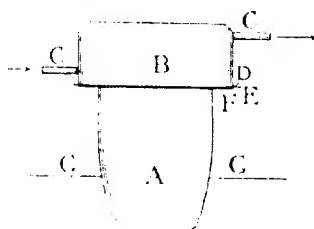
Some difficulty is experienced in fitting the gold cup or silver foil "mercury tight" to the crucible top, and the cooling water requires frequent renewal, as the collecting power of gold or silver is much reduced when warm. The author therefore employs a flat sheet of "fine" silver, which may be purchased of any thickness at about 3s. 6d. per ounce troy, and which, after annealing by warming to dull redness for a few seconds in a flame, may be rubbed perfectly flat between two surfaces of glass or wood. The silver may conveniently be somewhat thinner than a visiting-card, and is cut into a circular disc, F, about 2 inches in diameter, weighing from 2 to 6 grams according to its thickness. If of the former weight, it can be conveniently weighed on an assay balance, but it must be held up to the light and examined to insure absence of pin-holes, which often occur in thin foil, and which spoil the assay through escape of mercury. The crucible A may conveniently be of the deep form shown, and about 1¼ inches wide by 1¾ inches deep, and is ground down perfectly flat at the mouth on emery-paper. An ordinary Berlin porcelain crucible is used. A square plate, E, of silver foil about ¼ inch wider than the plate F is used as a cover. The plates E and F are kept cool by a round copper vessel, B, about 2 inches in diameter, with pipes, C, soldered in as shown for entrance and exit of the cooling water. The vessel B consists of a spun cap of copper soldered upon a flat copper disc with a turned up rim, D, which collects such water as occasionally condenses on the cooler. The copper may be about 1/16 inch thick. The top of a round tin box would serve equally well for the body, but it is advisable to have the bottom of copper on account of its high conductivity. A piece of tin, G, cut out to receive the crucible, localizes the heat around the crucible bottom and rests on an ordinary tripod stand.

The ore to be assayed is heated with iron filings free from grease. The filings are best prepared by heating a quantity of several pounds in a covered crucible to a fair red heat for about an hour. All grease, etc., having thus been driven off or

carbonized, the cooled crucible is opened : the top layer of the filings, if at all oxidized, is removed, and the filings are sifted. Those which pass through a 60-mesh sieve and those which pass a 30-mesh sieve are kept in separate stoppered bottles.

The ore is prepared by grinding it very finely, and may be dried before assay if containing no free mercury ; but if, as commonly happens, any native mercury is present in a finely-divided state, practically the whole of it may be lost in drying. In that case it must be assayed as received and calculated out on the dry weight. The loss of mercury in drying may be ignored in the determination of *moisture* in any ordinary ore, as it would scarcely affect the result even in the second decimal place.

The amount of ore to be taken for assay depends on its richness, as the silver foil has only a limited power of retaining mercury.

It is advisable to weight out : 2 grams if the ore contains under 1 per cent. of mercury ; 1 gram if the ore contains between 1 and 2 per cent. of mercury ; 0·5 gram if the ore contains between 2 and 5 per cent. of mercury ; 0·25 gram if the ore contains between 5 and 10 per cent. of mercury.

If the ore contains over 10 per cent. correspondingly less should be taken.

The ore is carefully mixed in the crucible with about 10 grams (roughly weighed) of the 60-mesh iron filings, and the mixture is covered with about 5 grams of the 30-mesh filings, even when only so small an amount as 0·25 gram of ore is used. The crucible is placed in the holder G on a tripod stand, the cleaned, flattened, weighed silver disc F is placed on the crucible with the disc E above to keep it clean, the cooler B is placed over all, and a weight is placed on the cooler to prevent displacement. Water supplied through a rubber tube traverses the cooler. A small Bunsen or spirit flame is brought beneath the crucible, the flame being of such a size as to just make the crucible bottom red, but so that the crucible is not red more than ¼ inch up the side. The heat is continued for twenty minutes, draughts being carefully excluded, as a draught may easily deflect so small a flame and practically stop the distillation. The iron removes the sulphur and also conducts the heat so that the mercury distils off and is collected by the disc F. After twenty minutes, the flame is removed, and after fifteen minutes' cooling the disc F is removed, dried by placing it in a water-oven for a few minutes, or by holding in tweezers and waving above a flame for a few seconds, cooled, and weighed. The assayer must decide for himself which method to use, and how long to allow for the drying. He should experiment on the disc from one of his assays by damping it, drying, and reweighing until he ascertains the conditions which insure drying without loss of mercury. When the ore contains bituminous matter, as sometimes happens, and as is shown by the smell or by a black or brownish stain on the foil, it is necessary to wash the foil with alcohol and dry as above before weighing.

Until the operator is experienced, it is advisable to reheat the crucible with another weighed piece of foil to insure that all the mercury has been driven off, but this is not usually found to be necessary. If the assay has been satisfactory, the mercury will all be seen as a dull or bright perfectly circular film on the foil, exactly the size of the crucible rim. If it extends beyond, which may occur either from too much

ore having been taken, so that the silver cannot properly retain the resultant mercury, or from careless flattening or adjustment of the foil, the assay must be repeated.

When first using the apparatus, the operator should experiment by repeatedly assaying the same sample, varying the temperature and time until he finds the conditions which yield the highest result. Half a dozen such tests, occupying in all not over three or four hours, will suffice for gaining perfect control over the method. By coupling together a number of coolers with rubber tubes and arranging a row of the assays on a bench, one may easily carry on a dozen assays at a time in a confined space. An inverted ½-gallon Winchester, fitted up like an inverted wash-bottle, and having a regulating clip on its indiarubber discharge tube, will suffice for cooling a battery of a dozen assays. The water leaving the last cooler should not feel more than lukewarm.

When the assayer is experienced, he can allow the distillation of one set to continue without watching, while weighing the discs from the previous set.

The special precautions to be observed are : (1) Avoidance of excessive heating of the crucible. The edge of the covering foil E should never feel warm to the fingers. (2) Cleanliness and perfect flattening of the silver foil F. (3) Careful adjustment of the foil and coolers and of the weights on the coolers to insure contact all round the crucible top. (4) Careful drying of the foil. (5) Avoidance of draughts. (6) Allowance of the full time mentioned (fifteen minutes) for cooling before removing the foil, lest uncondensed mercury vapour be lost.

Although gold has a greater affinity for mercury than silver possesses, and is therefore theoretically better, silver has a greater collecting power weight for weight, and a greater conductivity, and has been proved by comparative tests to give at least equally correct results. No comparative figures are given, because the results are identical within the limits of experimental error. Indeed, if anything, the new method gives slightly higher results.

The silver can be used an indefinite number of times, and appears, on account of its greater porosity after prolonged use, to improve.

When elaborate care is used, the method, as tested by diluting down a weighed small quantity of pure cinnabar or pure mercury sulphide or oxide, has been found extremely accurate, but under ordinary conditions a slight loss from leakage may be expected, and the difficulty of sampling such an ore as cinnabar renders the danger of error greater. The cinnabar is extremely heavy and the gangue is usually decidedly light, and the fact that cinnabar commonly occurs as little rich patches in the gangue even in the case of very low-grade ore, and is therefore practically freed during crushing, renders it extremely liable to settle, despite the most careful mixing, and to further accentuate the danger of inaccuracy through sampling. This danger is not great when the ore contains under 10 per cent. of mercury, and may be over-come with care ; but when the ore contains 20 per cent. or upwards, it is advisable to distil, say, 10 or 20 grams of the ore in a glass tube with iron filings by the old method already mentioned.

The error due to sampling is, of course, then only one-twentieth or one-fortieth of the probable error on a 0·5 gram sample, and the loss from leakage is practically nil. Such ores, however, seldom require to be assayed, and, as already stated, the

old method is practically impossible on average ores. With such low-grade ores it yields the mercury in beads so small that they can scarcely be collected and dried without heavy loss, and it is extremely cumbrous and slow.

On rich ores, the results by the author's method are sometimes too high and sometimes too low, either result being attributable to difficulty in sampling. As, however, the results are usually slightly low on ores containing over 20 per cent. of mercury when done without excessive precautions, the loss is probably due to leakage.

In the case of average ores, the total loss is so small as to be negligible, and duplicate results on a 1 per cent. ore should agree to within 0·05 per cent., a result which cannot be equalled by any wet method.

Experiments have been made in which the iron filings are replaced by reduced iron, or by copper, or by litharge, lime, etc.; but, apart from the extreme convenience of iron filings, the other materials have shown no advantage whatever, and litharge and lime are distinctly less effective.

The author is informed that the method works well with salts of mercury, and there is no apparent reason why it should not do so, although the iron filings would in some cases have to be replaced by one of the agents mentioned above, or by some other decomposing agent. He has, however, had practically no experience on this point.

The process has been employed in his laboratory for five or six years, and the apparatus has been sent to mercury mines in Russia, China, Italy, and British Columbia, where it has been in constant use. At two mines, the gold cup process which was then in use has been abandoned in its favour on account of its greater convenience and speed, and at all these mines it has been constantly employed for valuing, selling, or buying the crude ore, for assaying tailings, and for controlling the working of the furnaces, etc. The above description may therefore be taken as that of a proved rather than a suggested method of assay.

DISCUSSION.

The PRESIDENT (Mr. Bevan) asked if the process could be used on a larger scale than Mr. Holloway had indicated, using a larger quantity of the ore.

Mr. HOLLOWAY said that the use of a larger quantity of ore did not increase the accuracy of the method if one had a good balance; in fact, the process worked better with the small quantities recommended in the paper.

Mr. KITTO said that for many years he had used a gold cup having a fairly large cavity, and had found no difficulty in getting very accurate results without the addition of the ingenious apparatus which Mr. Holloway had described. He had been much interested in the device for automatically cooling the silver foil. Probably where, as in a mine, a large number of determinations had to be made, it would be very useful, but under ordinary circumstances he really did not think it necessary to complicate the very simple original apparatus. He had had no difficulty in getting the flange of the gold cup firmly fixed and accurately adjusted to the edge of the crucible.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

The Detection, Determination, and Rate of Disappearance of Form aldehyde in Milk. R. H. Williams and H. C. Sherman. (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1497.)—The authors find that by means of the potassium cyanide method (ANALYST, 1904, xxix., 5) formaldehyde in milk can be approximately determined at any concentration greater than 1 part in 160,000. They find that aqueous solutions of formaldehyde containing from 1 : 5000 to 1 : 40,000 lose steadily in strength on standing, the loss being not merely due to polymerization, but to actual destruction of the formaldehyde. Within the same limits, formaldehyde added to milk disappears about ten or twenty times as rapidly as from aqueous solutions of the same strength. Stronger solutions are much more stable; thus, an aqueous solution of 1 : 1,000 showed no appreciable loss after five months. From milk containing 1 part in 1,000 the rate of disappearance was the same as for an aqueous solution of 1 : 5,000. Souring of the milk does not affect the rate of disappearance. The hydrochloric acid and ferric chloride test is sensitive to a dilution of 1 : 250,000. Sourness of the milk does not affect the reaction. The test may be made more satisfactory by adding 50 to 75 c.c. of cold water to the milk after keeping it just below the boiling point for one minute as usual; the colour obtained in this case, however, is very fugitive. The gallic acid test is much more delicate than the ferric chloride test.   A. G. L.

Composition of the Fat of Pigs fed on Foods Rich in Oil. K. Farn steiner, K. Lendrich, and P. Buttenberg. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, xi., 1-8.)—The particular object of the present experiments was to ascertain whether the oily constituents of the fodder were deposited in the body fat of pigs fed on such fodder. The results show that the fat of pigs fed on cottonseed-meal gives a decided reaction with Halphen's reagent, but that the fat in no case contains phytos terol, and is consequently thus distinguished from lard adulterated with cottonseed oil. (*Cf.* ANALYST, 1904, p. 315.)   W. P. S.

On the Occurrence of Arsenic in Wines. H. D. Gibbs and C. C. James. (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1484.)—The authors have examined a total of 352 wines, some bottled and some in cask, and have found arsenic in 52 cases, in quantities ranging up to 1 part of arsenic in 2,500,000 of wine. Generally, however, the quantities found were much smaller than this. As probable sources of the arsenic they indicate the arsenical sprays used upon the vines, the sulphur burned for sulphuring the wine and receptacles, and, perhaps, also the lead-shot used in cleaning the bottles. The method used in testing for arsenic consisted in making the wine alkaline with milk of lime, evaporating to dryness, and igniting the residue at a low red heat. The ash was treated with sulphuric acid (1 to 3), the solution filtered

and introduced into the generator of a Marsh apparatus. As generator a 250 c.c. Florence flask was used, Kahlbaum's zinc and pure sulphuric acid being used to generate the hydrogen. The action was started by adding a few drops of platinic chloride. Immediately after adding the sulphuric acid the air in the apparatus was swept out by a rapid current of carbon dioxide, and the solution to be tested was then added. The evolved gas was passed through a spiral of lead acetate paper and then through calcium chloride, after which it entered a Jena glass tube of 0·7 cm. internal and 1·0 cm. external diameter drawn down to a constriction from 10 to 15 cm. long and 2 mm. external diameter. The tube was heated for a space of 16 to 15 cm., protected by wire gauze, before the constriction, the heating being continued for one hour. The electrolytic generator of Thorpe was also tried, but discarded because in some cases it failed to reveal the presence of any arsenic in wines known to contain arsenic.

A. G. L.

Process for Determining the Quality (Fineness) of Flour. N. Wender.

(*Zeit. Untersuch. Nahr. Genussm.*, 1905, x., 747-756.) -Wheat and other grains contain an enzyme capable of liberating oxygen from hydrogen peroxide, and upon the fact that this enzyme resides principally in the embryo and outer portions of the grain, the author bases a process for distinguishing between best white flour and other flours containing more or less bran or inferior flour. It is recognised that, taken by itself, the colour of flour is no criterion in judging whether a sample is best quality, "seconds," "thirds," etc. The process is carried out as follows: 25 grams of the flour are rubbed down with 100 c.c. of water until free from lumps and then rinsed into a flask with a further 100 c.c. of water. The flask is closed by an indiarubber stopper carrying a tapped funnel and a delivery tube connected to a measuring-tube filled with water. Ten c.c. of hydrogen peroxide are then introduced through the funnel, and the action allowed to proceed for about thirty minutes at a temperature of 20 C. The volume of the liberated gas is then read off. The following examples are given, in which the results are calculated for 100 grams of meal: Wheat starch, 8 c.c.; wheat flour, 169 c.c.; wheat bran, 342 c.c.; rye flour, 153 c.c.; rye bran, 339 c.c.; maize flour, 389 c.c. In a series of flours of decreasing quality, the finest flour gave 128 c.c., and the coarsest 486 c.c. The author admits that many more analyses must be made before any degrees of quality can be fixed by this method, but considers that the latter will be of use when the flours of different countries, mills, etc., have been examined and classified. W. P. S.

A New Adulterant of Lemon-Juice. H. Matthes and F. Müller. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, xi., 20, 21.) A sample of so-called lemon-juice gave the following results: Alcohol, by weight, 5·43 per cent.; total solids, 13·47 per cent.; total acidity, as citric acid, 8·19 per cent.; mineral matter, 0·205 per cent.; alkalinity of ash, 0·49 c.c. acid; phosphoric anhydride, 0·05 per cent.; polarization after distillation, +4·5 in 100 mm. tube. The sample contained starch-syrup, evidently

* It has been shown that the use, in this way, of platinic chloride is inimical to the correct estimation of arsenic. Cf. Chapman, this vol., p. 3. - EDITOR.

added to imitate the pectinous substances of pure lemon-juice and the amount of phosphoric anhydride found was probably due to the addition of a salt of this acid.

W. P. S.

Composition of Lemonade Essences. Utz. *(Zeit. offentl. Chem.*, 1906, xii., 12-13.)—The liquids to which the following analyses refer are sold for the purpose of making lemonade and similar drinks by diluting the liquid with water, soda-water, etc. They consist essentially of an aqueous solution of tartaric or citric acid, to which an alcoholic solution of certain flavouring substances (esters) are added. The figures express grams per 100 c.c. :

	Raspberry Essence A	Raspberry Essence B.	Lemon Essence A.	Lemon Essence B.
Alcohol	14·55	19·40	19·91	27·84
Total solids	10·11	11·60	18·54	9·74
Mineral matter	0·065	0·174	0·082	0·119
Total acidity, as tartaric	8·029	11·56	15·57	9·38
Sugar...	none	none	none	none

All four samples were strongly coloured with coal-tar dyes, and two of them— Raspberry Essence B and Lemon Essence B—contained not inconsiderable quantities of saponin.

W. P. S.

On the Colouring Matter of Saffron. F. Decker. *(Chem. Zeit.*, 1906, xxx., 18.)—Crocetin, the colouring matter of saffron, has hitherto only been isolated in an amorphous form, since the readiness with which it resinified prevented its being obtained in a crystalline condition. The author, however, has succeeded in obtaining crocetin crystals of constant composition by digesting the resin-free solution of the colouring matter in very dilute sodium hydroxide solution at 60° to 70° C., with an excess of ammonium carbonate solution. The ammonium compound of crocetin was deposited from the liquid on cooling, in the form of yellow needles, which dissolved readily in alkalies, but were only sparingly in water and alcohol. The addition of ammonium carbonate to any of these solutions reprecipitated quantitatively the crocetin compound. An elementary analysis gave the following results : Carbon, 64·60 ; hydrogen, 8·70 ; nitrogen, 8·06 ; and oxygen, 18·64 per cent. C. A. M.

Separation of the Conium Alkaloids. J. von Braun. *(Berichte*, 1905, xxxviii., 3108-3113 ; through *Pharm. Jour.*, 1905, vol. 75, 909.)—The separation of the alkaloids of the hemlock—namely, coniine, methyl-coniine, γ-coniceine, conhydrine, and pseudo-conhydrine, may be effected as follows : The greater portion of the coniine, which forms the chief constituent, is separated by distillation and the residue then fractionated up to 190° C., whereby the conhydrine (m.p. 118° C.) remains as an undistilled residue. The lower fractions are next benzoylated in alkaline solution, and the resulting oil, after dissolving in ether, is extracted with acid to remove the

methyl-coniine. The ethereal solution is then concentrated and treated with petroleum spirit (ligroin) to precipitate the benzoyl-amino-butyl-propyl-ketone, which is formed by the action of benzoyl chloride on γ-coniceine. The mother-liquor is redistilled and yields benzoyl coniine (b.p. 203°to 204° C. at 16 mm. pressure), and some more of the benzoyl-amino-ketone. Starting with 104 grams of material, the author was able to obtain 1 gram of conhydrine, 7 grams of methyl-coniine, 52 grams of amino-ketone corresponding with 26 grams of γ-coniceine, and 124 grams of benzoyl-coniine, corresponding with 68 grams of coniine, total 102 grams. The coniine recovered from the benzoyl derivative proved to be a mixture consisting of *l*-coniine and a little *d*-coniine. The substance described above as methyl-coniine has [α]$_D$ 35·66 at 24° C., and appears to be a simple substance. It yields a picrate melting at 114° C., a platinichloride melting at 195 C., and an aurichloride between 80° and 90 C. W. P. S.

The Oleoresin of Pinus Longifolia. F. Rabak. (*Pharm. Rev.*, 1905, xxiii., 229; through *Pharm. Jour.*, 1906, vol. 76, 11.)—The oleo-resin of *Pinus longifolia*, a native of the lower Himalayas, is a white, opaque, tough substance showing a partially crystalline structure. Its odour is lemon-like. A sample examined had a specific gravity of 0·866 and [α]$_D$ + 2° 48'. It yielded 18·5 per cent. of essential oil on distillation, the oil having a characteristic pinene odour, and a faint aroma of limonene. On fractionation, dextropinene and lævolimonene were isolated. The residual resin was whitish and brittle; it had an acid value of 112 and ester value of 13. When dissolved in acetic acid the solution deposited crystals of a resin acid melting at 138° to 140° C. W. P. S.

A Distinctive Reaction for Euphorbium Resin. A. Tschirch and Paul. (*Pharm. Zeit.*, 1905, l., 561; through *Pharm. Journ.*, 1906, vol. 76, 35.)—About 0·01 gram of the resin is treated with 10 c.c. of petroleum spirit, and the mixture filtered. The filtrate is allowed to flow on to the surface of 20 c.c. of sulphuric acid, to which 1 drop of nitric acid has been added. A red-coloured zone is obtained at the junction of the two liquids; on shaking, the acid layer becomes red and, in the course of a day or two, turns brown. W. P. S.

Estimation of Formaldehyde in Formaldehyde Pastilles (Trioxymethylene). Ernst Rüst. (*Zeit. angew. Chem.*, xix., 138.)—The author claims the following method of estimating formaldehyde to be superior to the older ones: Two grams powdered trioxymethylene are added to a 250 c.c. Erlenmeyer flask, in the neck of which is fitted a funnel. The solid is washed in with 70 c.c. normal sodium hydroxide solution. To this mixture 9 to 10 grams of 30 per cent. hydrogen peroxide is added slowly at first to prevent undue heating. After standing for two hours the mixture is warmed gently to boiling, to decompose the excess of hydrogen peroxide. The funnel, after being carefully washed with water, is removed, a small excess of normal sulphuric acid solution added, and the mixture titrated back with normal sodium hydroxide solution, using phenolphthalein as indicator. One c.c. of normal sodium hydroxide corresponds to 0·03 gram CH$_2$O. The original substance

must be tested for alkalies or acids before this method is applied, and these must be taken into account in the final calculation.   H. D. L.

The Detection of Iodine Compounds in the Dry Way. B. Merk. (*Pharm. Zeit.*, 1905, l., 1022; through *Chem. Zeit. Rep.*, 1905, xxix., 405.)—The substance under examination is rubbed with a little potassium persulphate and some soluble starch, the mixture becoming more or less blue in the presence of iodine compounds not containing oxygen:

$$2KI + K_2S_2O_8 = 2K_2SO_4 + I_2.$$ C. A. M.
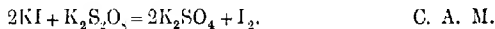
TOXICOLOGICAL ANALYSIS.

Toxicology of Atropine. C. Ipsen-Innsbruck. (*Zeit. angew. Chem.*, xix., 141.)—The author has investigated the stability of atropine in the presence of decomposing organic matter, the method of absorption of this alkaloid in, and excretion from, living organisms. The results, which are opposed to those of previous investigations, are summarized in the following manner: Atropine is rapidly absorbed by all parts of the body and distributed in the blood. The separation rapidly follows from all the natural outlets, lasting from three to fourteen days, depending on the animal. Further, 0·03 gram atropine, after standing for twelve years in contact with decomposing blood, beer, and other organic bodies, can still be detected.   H. D. L.

Toxicity of Eggs when administered Hypodermically. G. Loisel. (*Comp. Rend.*, 1905, cxli., 730; through *Pharm. Journ.*, 1906, vol. 76, 65.)—Eggs are found to be by no means free from toxicity when administered hypodermically. The lethal dose for rabbits of the emulsion of yolk of ducks' eggs with water is 10 c.c. per kilo of body-weight. A 10 per cent. solution of the dried yolk in saline water is similarly toxic by intravenous injection in doses of 80 c.c. Hens' eggs are slightly less toxic, and turtles' eggs from Mauritius somewhat more so. In fact, all three are markedly poisonous when injected either into the veins, or hypodermically, or into the peritoneal cavity. The symptoms which precede death indicate that the nervous system is profoundly affected by the poison.   W. P. S.

ORGANIC ANALYSIS.

Preparation of Pure Ethyl Alcohol. L. W. Winkler. (*Berichte*, 1905, xxxviii., 3612-3616; through *Pharm. Journ.*, 1905, vol. 76, 12.)—Acetaldehyde is removed from commercial absolute alcohol by allowing the sample to stand over finely-powdered silver oxide for several days, a little potassium hydroxide being also added. The amount of silver oxide required is never more than a few grams per litre, and about 1·2 grams of potassium hydroxide is sufficient to neutralize all the acetic acid resulting from the oxidation of the aldehyde. The mixture should be shaken from time to time. The water present in the alcohol is then removed by heating the latter for several hours over, and finally distilling from, metallic calcium

filings, using about 20 grams of the metal per litre. The alcohol so obtained can be once more distilled from metallic calcium. The advantage in the use of calcium over sodium lies in the fact that calcium hydroxide is totally insoluble in alcohol, and therefore as long as the alcohol contains moisture a white precipitate will be formed.

The author has made a number of determinations of the specific gravity of pure ethyl alcohol, and has deduced from them the following formula for calculating the specific gravity of alcohol at any temperature from 0° to 30° C.:

$$\text{Specific gravity } 0°-30° = 0·80629 - 0·0008381t - 0·0000004t^2,$$

where 0·80629 is the specific gravity of alcohol *in vacuo* compared with that of water at 4° C. The boiling-point of pure alcohol was found to be 78·37° C. at 760 mm. pressure. It was observed that absolute alcohol is not so hygroscopic as is commonly imagined; 200 c.c. of absolute alcohol absorbed less than 0·1 per cent. of water after fifteen minutes' exposure to the air. W. P. S.

The Determination of Traces of Benzaldehyde. H. Hérissey. *(Journ. Pharm. Chim., 1906, xxiii., 60-65.)*—Phenylhydrazine reacts with benzaldehyde to form an insoluble phenylhydrazone—

$$C_6H_5NH.NH_2 + C_6H_5.COH = C_6H_5.CH.N.NH.C_6H_5 + H_2O.$$
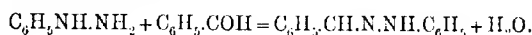
The reagent used by the author consisted of 1 c.c. of freshly distilled phenylhydrazine and 0·5 c.c. of glacial acetic acid in 100 c.c. of water. On treating an aqueous solution of benzaldehyde with an equal volume of this reagent, and allowing the mixture to stand for twenty-four hours at 15° to 20° C., there was formed an insoluble crystalline precipitate, which could be collected in a Gooch's crucible, washed with a known quantity of cold water, and dried in a vacuum over sulphuric acid until constant in weight. It was found, however, that very faint traces of the aldehyde required a very long time for complete combination, and, on the other hand, the results were liable to be too high if the reagent was allowed to act for several days. But by heating the mixture on the boiling water-bath for twenty minutes, and then allowing the liquid to stand for twelve hours before filtration, washing the precipitate in the Gooch's crucible with 20 c.c. of water and drying it *in vacuo*, excellent results were obtained, especially when the quantity of phenylhydrazone did not exceed 0·1 to 0·25 gram. C. A. M.

On the Determination of Sugar with Fehling's Solution. F. P. Lavalle. *(Chem. Zeit., 1906, xxx., 17.)*—It is often difficult to determine the end-point of the reaction in titrating a solution of glucose, owing to the cuprous oxide subsiding but slowly, and reflecting its colour to the surface. The author obviates this by adding an excess of alkali, and thus preventing entirely the separation of the cuprous oxide. From 5 to 10 c.c. of Fehling's solution are placed in a 200 c.c. porcelain basin, together with 30 c.c. of sodium hydroxide solution (1 : 3) and 50 to 60 c.c. of water,

and the liquid heated to incipient boiling, and then titrated with the sugar solution, the reaction being complete as soon as the last drop causes the blue colour of the Fehling's solution to disappear. Test experiments are stated to have given very satisfactory results.   C. A. M.

The Detection and Determination of Trehalose by Means of Trehalase.
P. Harang. (*Journ. Pharm. Chim.*, 1906, xxiii., 16-20.)—The method is based upon the fact that trehalose ($a = +197°$ 3') is inverted by the specific enzyme trehalase into two molecules of glucose, which will, of course, reduce Fehling's solution. Thus, if a 1 per cent. aqueous solution of anhydrous trehalose giving in the polarimeter a reading of $a = +3°$ 57' be treated with trehalase, the liquid, after complete inversion of the hexabiose, will be found by means of Fehling's solution to contain a quantity of reducing sugar corresponding to 1·052 grams of glucose, and the deviation ($l = 2$) will be $+ 1°$ 6', a difference of 2 51'. If, then, the difference between the rotations calculated from the amount of glucose formed under the action of the enzyme coincides with the polarimetric readings, the presence of trehalose may be inferred, and its amount may be calculated, provided that the enzymic action is complete.

In order to obtain the specific enzyme trehalase the author incubates a cultivation of *Aspergillus niger* on Raulin's fluid at 33° C. until the first signs of fructification (about twenty-four hours). The nutrient fluid is then decanted and replaced with water, and the cultivation allowed to stand at the ordinary temperature for five or six days until fructification appears, the water being renewed every twenty-four hours. The mould fungus is then pressed between filter-papers, finely divided, left for three hours in contact with a fourth of its weight of 95 per cent. alcohol, drained with the aid of a filter-pump, and finally dried in the oven at 33° C. and powdered. This preparation has a strong enzymic action upon trehalose, 0·5 gram being sufficient to invert 1 gram of the sugar in 100 c.c. of water within forty-eight hours at 33° C.

Before using the enzyme for the detection of trehalose in mushrooms, etc., it is necessary to eliminate substances such as glycogen, which can also be attacked by it. The fungi are twice extracted, as soon as possible after being gathered, for ten minutes with their own weight of boiling 80 per cent. alcohol, and the united extracts filtered. The filtrate is distilled under reduced pressure until the residue is only 100 c.c. (from 1 kilo of fresh mushrooms). On now adding 4 parts by volume of 80 per cent. alcohol to the residue there is an abundant precipitate, which is left to subside until the next day. The clear liquid is then decanted, and the residue mixed with a few c.c. of water, taken up with 4 parts by volume of 80 per cent. alcohol, and boiled for twenty minutes on the water-bath under a reflux condenser. It is then allowed to cool and the supernatant liquid decanted, united with the washings, and evaporated to dryness *in vacuo*. Finally, the residue is taken up with water saturated with thymol (100 c.c. for each 200 grams of mushrooms), and this solution treated with enzyme.   C. A. M.

The Characteristics of Certain Animal Fats. C. Schneider and S. Blumenfeld. (*Chem. Zeit.*, 1905, xxx., 53, 54.)—The following physical and chemical values were obtained :

Animal	Fats							Fatty Acids						
	Specific Gravity at 15° C.	Refractometer.	Acid Value.	Saponification Value.	Iodine Value (Hübl).	Hehner Value.	Reichert-Meissl Value.	Specific Gravity at 15° C.	Refractometer.	Melting-point, °C.	Solidification-point, °C.	Neutralization Value.	Iodine Value.	Acetyl Value.
Vikare seal (Phoca fœtida)	0·9321	87·0 at 20° C.	0·48	188·5	191·35	95·6	1·55	0·9172	74·1 at 20° C.	14·0	13·0-14·0	196·0	195·3	—
Vikare seal (Phoca fœtida)	0·9336	—	1·08	189·0	193·3	95·8	0·96	—	—	—	13·0-14·0	196·0	204·8	—
Porpoise (Phocæna communis)	0·9334	62·7 at 25° C.	1·2	224·8	111·2	85·5	42·4	0·9121	54·3 at 25° C.		18·0	207·0	126·0	4·55
Coot (Fulica atra)	0·9163	62·9 at 25° C.	1·66	192·6	87·13	95·2	0·35	0·9151	44·7 at 35° C.	33·5-34·5	30·5	—	84·8	—
Crane (Grus cinerea)	0·9222	61·5 at 20° C.	9·33	191·2	75·25	95·7	0·13	0·9005	10·5 at 30° C.	31·0	29·3	201·0	73·5	1·35
Lynx (Lynx europæus)	0·9248	70·0 at 20° C.	0·81	190·2	110·6	95·8	0·43	0·9412	53·9 at 35° C.	35·5	35·0	202·7	111·5	7·67
Glutton (Gulo borealis) body fat	0·9153	54·2 at 30° C.	5·84	193·3	54·36	95·4	0·12	0·9115	31·9 at 45° C.	40·0-41·0	37·5	203·4	55·5	3·0
Glutton (Gulo borealis) kidney fat	0·9230	45·2 at 45° C.	—	193·3	50·82	95·8	—	—	31·7 at 45° C.	40·0-41·0	—	203·0	52·8	—
Bear (Ursa arctos)	0·9156	60·8 at 20° C.	30·6	191·0	80·7	94·5	0·33	0·9347	43·0 at 40° C.	37·5	36·1	203·0	76·5	5·7

The high Reichert value of the porpoise fat was due to the presence of a considerable quantity of the glycerides of valeric acid. The fat, which was derived from the body, was oily, and had a pale yellow colour. Of the other fats examined, that of the seal was a soft yellow semi-solid; the fats of the coot, crane, and lynx were soft white or light yellow semi-solid masses; the fat of the glutton was a white, not very hard fat; and the bear's fat had the consistency of vaseline at 15° C. It is pointed out that the iodine value of the fat of the lynx is the highest yet recorded for land beasts of prey.   C. A. M.

Determination of the Total Organic Acids in Tobacco. J. Tóth. *(Chem. Zeit.,* 1906, xxx., 57, 58.)—The method proposed is similar to the one described previously by the author for the determination of nicotine (ANALYST, 1902, p. 12). Two grams of the dry powdered tobacco are moistened with 2·5 c.c. of 20 per cent. sulphuric acid, and then mixed with sufficient plaster of Paris to form a dry powder. This is placed in a well-corked cylinder and shaken for forty-eight hours with 100 c.c. of anhydrous ether; 50 c.c. of the ethereal solution are then drawn off, evaporated slowly, and the residue dissolved in warm water. The solution is now titrated with $\frac{N}{2}$ sodium hydroxide solution, using alkanna tincture as indicator (ANALYST, 1903, p. 193), and the result calculated into anhydrous oxalic acid. In thirty-two samples of various tobaccos examined, the writer found from 3·6 to 8·7 per cent. of total organic acids (expressed as oxalic acid), and the quantity of organic acid was found to be proportional to the burning quality of the several tobaccos—that is, bad-burning tobaccos contained the most acid.   W. P. S.

Estimation of Tannin in Crude Products. A. Manea. *(Chem. Zeit. Rep.,* 1905, xxix., 381.)—The principle of the method lies in the fact that when a certain quantity of a tannin solution is added to a mixture of a known quantity of glacial acetic acid and neutral lead acetate of known dilution, the tannin alone is precipitated with the lead, whilst all other substances remain in solution. The author has obtained results which give not more than 0·5 per cent. difference in analyses of the same raw material.   E. K. H.

Estimation of Caoutchouc. T. Budde. *(Chem. Zeit. Rep.,* 1905, xxix., 393.) —The process recommended, after many experiments, is as follows: A solution of bromine in carbon tetrachloride is used as a brominating liquid, iodine being added as a halogen carrier, the action being then continuous. The proportions used by the author are: 16 grams bromine (6 c.c.) and 1 gram iodine dissolved in carbon tetrachloride and made up to 1 litre. For the estimation about 1 gram of the sample of caoutchouc is placed in a 100 c.c. flask, covered with carbon tetrachloride, and allowed to stand, with frequent shaking, until the caoutchouc has dissolved, or is evenly divided. The flask is then filled to the mark and well shaken. Ten c.c. are taken for each analysis. This is filtered, if necessary, in an Allihn's tube and washed with about 50 c.c. CCl₄. (If the solution is too viscous, it must be diluted.) To the filtrate 50 c.c. of the brominating solution are added, when a jelly-like substance is soon precipitated. After the solution has become clear (quarter of an hour), half its

volume of alcohol is added; the liquid is now clear yellow, and the tetrabrom-caout-chouc is transformed into the white form. It can now be easily transferred to a weighed filter paper, washed first with a mixture of 2 parts carbon tetrachloride and 1 part alcohol, and then with pure alcohol, and dried to constant weight at 60° C.; 450 grams of tetrabrom-caoutchouc = 136 grams of pure caoutchouc. Caoutchouc resin and oxidized caoutchoucs do not take part in the bromine reaction. The process recommends itself by its simplicity, and especially by the fact that it gives the true content of pure caoutchouc.
L. K. H.

The Direct Determination of the Acetyl and Benzoyl Groups. R. Meyer and E. Hartmann. (*Berichte*, 1905, xxxviii., 3956.)—From 0·5 to 0·7 gram of the substance is heated with about 5 grams of pure sodium hydroxide and as small a quantity as possible of methyl alcohol which has been purified by distillation with potassium hydroxide. After about an hour the saponification is complete in the case of most acetates, and the solution is then mixed with 50 c.c. of phosphoric acid (specific gravity 1·104), and distilled in a current of steam, a little lime being placed in the vessel in which the steam is generated. In order to determine whether the distillation is complete, portions of the distillate are titrated from time to time after it is thought that the bulk of the acid has passed over. The distillation should be continued until 150 c.c. of the distillate consume not more than 1 or 2 drops of $\frac{N}{10}$ baryta solution, phenolphthalein being used as indicator. The determination of the benzoyl group is carried out in the same way, and gives equally satisfactory results.
C. A. M.

INORGANIC ANALYSIS.

Provisional Methods for Copper, Lead, and Zinc of the Committee on Uniformity in Technical Analysis of the Western Association of Technical Chemists and Metallurgists. (*Chem. Engineer*, 1905, ii., 287.)

Copper.—The iodometric method is used, the sodium thiosulphate solution (20 grams per litre) being standardized by dissolving 0·2 to 0·5 gram of copper foil in 5 c.c. of nitric acid and evaporating to 2 or 3 c.c.; after adding 5 c.c. of hot water and 6 c.c. of ammonia, the whole is boiled for a few minutes, cooled, and diluted to 75 or 80 c.c. After adding 8 c.c. of acetic acid and 10 c.c. of potassium iodide solution (30 per cent.), and well shaking, the liquid is titrated with the thiosulphate, 4 or 5 c.c. of starch solution (1 gram per 200 c.c.) being added after the colour has been changed from brown to yellow. To determine copper in ores, 0·5 gram of the sample is heated with 2 c.c. of nitric acid, 3 c.c. of hydrochloric acid, and 4 c.c. of sulphuric acid, until white fumes are evolved. After cooling and diluting with 25 c.c. of water, the whole is boiled with a piece of sheet aluminium; 10 c.c. of hydrogen sulphide water are then added to insure complete precipitation, and the precipitate filtered off, washing three times by decantation; 55 c.c. strong nitric acid are then poured over the copper and aluminium; the aluminium is removed and washed with a little hot water, and the filter washed with strong bromine water. The solution is then

evaporated down to 2 or 3 c.c.; 5 c.c. of hot water and 6 c.c. of ammonia are added; the whole is boiled, acidulated with 8 c.c. of acetic acid, and titrated as above.

Lead. — The ammonium molybdate method is used. To standardize the solution, 0·3 to 0·5 gram of lead foil is dissolved in 10 to 15 c.c. of 1·2 nitric acid; 20 c.c. of 1·1 sulphuric acid are then added; the whole is well stirred and allowed to settle. The liquid is then decanted off through a filter, and the precipitate washed three or four times with 2 per cent. sulphuric acid, and finally once with cold water. The filter is then washed free from lead sulphate by repeatedly passing 50 c.c. of a hot 20 per cent. ammonium acetate solution through it, and finally washing with hot water. The solution is then heated with the main bulk of the precipitate until the latter is dissolved, when it is diluted to 200 c.c. made just acid with acetic acid, and titrated with ammonium molybdate solution (8·64 grams per litre) until a drop of the liquid gives a yellow colour with a drop of tannic acid solution (1 gram in 300 c.c. water). For ores, 0·5 to 1 gram is heated with 10 c.c. of strong nitric acid and 10 c.c. of strong sulphuric acid until white fumes appear, when the liquid is cooled, diluted to 50 c.c., boiled, and treated as above.

Zinc.—The ferrocyanide method is used. To standardize the solution 0·2 to 0·3 gram of freshly-ignited zinc oxide is dissolved in 10 c.c. of hydrochloric acid, and neutralized with ammonia; 6 c.c. of hydrochloric acid are then added; the liquid is diluted to 180 c.c. with water, boiled, and titrated as follows: The solution is divided into two equal parts; one of these is titrated quickly, after which the other part is added, and the titration finished by adding nearly enough of the ferrocyanide solution at once to precipitate the zinc, and then very carefully adding the solution until a yellow colour is obtained with a drop of uranium acetate solution containing 4·5 grams in 100 c.c. of water. The ferrocyanide solution contains 21·6 grams per litre. For ores, 0·5 to 1 gram is dissolved in 4 to 8 c.c. of hydrochloric acid, and an equal amount of nitric acid. The solution is evaporated down to one-third its volume; any gelatinous silica separated is filtered off, and the filtrate evaporated to dryness with 15 c.c. of a saturated solution of potassium chlorate in nitric acid. Without any baking, the residue is boiled with 40 c.c. of a solution made by dissolving 60 grams of ammonium chloride in 250 c.c. of water and 150 c.c. of concentrated ammonia. The precipitate obtained is filtered off and washed with the same ammonium chloride solution; if much iron is present, the precipitate is dissolved in the minimum of hydrochloric acid, and reprecipitated with the ammonium chloride solution. The filtrate is neutralized, 15 c.c. of hydrochloric acid and 15 grams of granulated lead are added, and the whole is boiled until all the copper is precipitated, after which the titration is made as above. All the conditions should be the same in all titrations, as far as possible. The temperature should always be near the boiling-point.   A. G. L.

The Volumetric Determination of Lead as Iodate. L. Moser. (*Chem. Zeit.*, 1906, xxx., 9.)—On treating a solution of a lead salt with potassium iodate in moderate excess, there is formed a heavy crystalline precipitate of lead iodate, which is nearly insoluble in water, and only sparingly soluble in nitric acid, but dissolves readily in hydrochloric acid with the formation of chlorine. This lead iodate is

much more insoluble than the sulphate, and good results can be obtained in analytical determinations based on the reaction. The solution of the lead salt, which may contain acetic acid or a little nitric acid, is treated with a measured quantity of standard potassium iodate solution, made up to a definite volume, and shaken, and the lead iodate allowed to subside. An aliquot portion of the clear supernatant liquid is then titrated with thiosulphate solution, after the addition of potassium iodide and dilute sulphuric acid. The excess of iodate thus determined is subtracted from that originally added, and the difference corresponds to the amount of lead present, 2 parts of potassium iodate being equivalent to 1 part of lead.

In examining commercial sugar of lead, 1 gram of the sample is dissolved in water, mixed with 70 c.c. of decinormal potassium iodate solution, and made up to 200 c.c. An aliquot portion (50 c.c.) of the clear supernatant liquid is then treated with potassium iodide, and the liberated iodine titrated with standard thiosulphate solution. The amount of iodine found corresponds to the amount of free acid in the sugar of lead. Sulphuric acid is now added, and the main quantity of iodine titrated. When the original sample does not yield a clear solution, a few drops of acetic acid are added to dissolve basic salts, etc. C. A. M.

The Rapid Precipitation of Antimony Electrolytically. Julia Langness and Edgar F. Smith (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1524.)—In consequence of Fischer and Boddaert's objections (*Zeits. f. Elektrochemie*, x. 950), the authors have repeated Exner's work on the deposition of antimony, using the rotating anode (ANALYST, 1903, xxviii., 330), and they find the method to give excellent results. They used an almost boiling solution of a total volume of 70 c.c., containing 0·24 gram of antimony in either state of oxidation, as well as 15 c.c. of sodium sulphide solution (specific gravity, 1·18), 3 grams of potassium cyanide, and 1 c.c. of 10 per cent. sodium hydroxide. Only 2 grams of potassium cyanide need be added if only 10 c.c. of sodium sulphide solution are present. The current was 6 ampères per 100 sq. cm. at 3·5 to 4 volts, the time being fifteen minutes. The method may be applied to the analysis of stibnite, the ore being directly treated with sodium sulphide, and to the separation of arsenic from antimony. In six experiments in which 0·1268 gram of antimony and 0·2000 gram of arsenic were present, the maximum error on the antimony was 0·0001 gram. A. G. L.

The Determination of Bismuth and its Separation from other Heavy Metals. H. Salkowski. (*Berichte*, 1905, xxxviii., 3913, 3914.)—It was suggested by the author in 1868 that it would be preferable to determine bismuth in the form of a phosphate rather than as an arsenate, and he has now worked out the details of the method. The precipitate can be ignited without fear of reduction and weighed as $BiPO_4$. It is essential that the solution should not contain hydrochloric acid or chlorides, and that free nitric acid should not be present in any considerable quantity. Good results are stated to have been obtained in this way in the separation of bismuth from copper and lead, but the details are not described. C. A. M.

The Iodometric Determination of Copper. T. Brown, Jun. (*Chem. Engineer*, 1905, ii., 307.)

—The method described consists in dissolving from 2·5 to 0·5 gram of the ore in *aqua regia*, evaporating the solution with sulphuric acid, filtering from gangue and lead sulphate, and precipitating the filtrate with sodium thiosulphate. In precipitating with thiosulphate the author recommends boiling the liquid for one half hour for high-grade ores, and for one hour or even longer for low-grade ores ; if too much evaporation takes place, water should be added. The precipitate is filtered off, washed with hot water, and roasted to oxide at a dull red heat. The copper oxide obtained may contain antimony, bismuth, and silver. It is placed in an 8-ounce flask, nitric acid, water, and about 0·5 gram of potassium chlorate are added, and the whole is boiled down to about half its original volume. Should any chlorate become decomposed a little water is added, and the chlorine liberated boiled off. After cooling, a little water and a slight excess of ammonia are added, and the whole is boiled again for a few minutes ; this treatment insures a more distinct end-point. The solution is then acidified with acetic acid, the determination finished as usual with potassium iodide and standard thiosulphate solution.

A. G. L.

Analysis of Tungsten-Tin Minerals. Henri Angenot. (*Zeit. angew. Chem.*, xix., 140.)

—On account of the extreme difficulty experienced in the estimation of stannic oxide and tungstic acid in presence of each other, the author has introduced the following modification of the Bornträger method : One gram of the finely powdered mineral is carefully fused with sodium peroxide in an iron crucible for a quarter of an hour. This is digested with water and made up to 250 c.c. If lead be present, it must be separated with carbon dioxide and the mixture finally filtered. One hundred c.c. of the filtrate are treated with a mixture of 15 c.c. nitric acid and 15 c.c. hydrochloric acid, and then evaporated to dryness. The residue is dissolved in a mixture of 100 grams ammonium chloride, 100 grams hydrochloric acid, and 1,000 c.c. water, and filtered. The undissolved tungstic acid is dissolved in warm ammonia, and the process repeated, and the insoluble product finally ignited.

A second 100 c.c. is used for the estimation of the tin. Two to three grams of zinc are added, and the whole allowed to stand for one hour at 60° C., then filtered from the precipitated oxide of tungsten, and the filtrate treated with sulphuretted hydrogen to remove the tin, which is weighed as sulphide. H. D. L.

The Separation of Iron from Zinc. V. Komar. (*Chem. Zeit.*, 1906, xxx., 31, 32.)

—The zinc and iron salts are converted into sulphates, dissolved in sulphuric acid (specific gravity, 1·3), and the solution oxidized by the addition of a little nitric acid. The mixture is then evaporated, at first on the water-bath, then on the sand-bath, and the residue finally heated over a free flame, care being taken to avoid crepitation. After igniting at a dull-red heat, the residue is dissolved in water and the ferric oxide collected on a filter, washed, and weighed, Zinc sulphate does not decompose at a temperature of 700° C., or more. W. P. S.

Standardizing Potassium Permanganate for Iron Determinations. Richard K. Meade. (*Chem. Engineer*, 1905, ii., 281.)—As a standard for permanganate solutions, the author prefers to use pure electrolytic iron. This is obtained by electrolysing, in a glass beaker, a solution containing 0·5 gram of iron as pure ferrous or ammonium ferrous sulphate dissolved in 250 c.c. of saturated ammonium oxalate solution. The anode is formed of a centrally-placed piece of platinum wire, the cathode consisting of two pieces of platinum foil 1½ inches square. After electrolysing for two hours with a current of from 0·5 to 0·7 ampère, about 0·15 gram of iron will be deposited on each piece of foil. After weighing each piece is dissolved separately in a mixture of 500 c.c. water and 50 c.c. of sulphuric acid, which has been previously boiled for some time, whilst a current of carbon dioxide was led through it. The flask and the dissolved iron are allowed to cool in the current of carbon dioxide, and titrated as usual. Proceeding in this way, it is found that the iron value of apparently pure iron wire is often above 100 per cent. A. G. L.

The Use of Ammonium Persulphate in the Determination of Chromium in Steel. Harry E. Walters. (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1551; and *Proc. Eng. Soc. West Pennsylvania*, 1905, xxi., 465.)—The method consists in determining chromium and manganese together, after oxidation by ammonium persulphate, by means of ferrous sulphate, and determining the manganese separately by means of sodium arsenite : 1·25 grams of the sample are dissolved in 35 c.c. dilute sulphuric acid (1 : 5), a small amount of ammonium persulphate being added to oxidize the iron and carbonaceous matter; the liquid is diluted to 100 c.c., 40 c.c. of silver nitrate solution (containing 0·16 gram of the salt), and then 5 to 7 grams of slightly moist ammonium persulphate are added, and the whole is boiled for five minutes, after which the liquid is cooled and made up to 500 c.c. On 100 c.c. of this solution the manganese is then determined by titrating in a porcelain dish with sodium arsenite solution, made up according to Blair, and standardized against a chrome steel of known manganese content. To the remaining 400 c.c. a measured volume of ferrous sulphate solution (22·5 grams of ferrous sulphate and 50 c.c. of strong sulphuric acid per litre) is added, and the excess of ferrous sulphate determined with standard permanganate solution (1·82 grams of the salt per litre). The latter may be standardized against iron or against a pure chromium salt; it should be compared with the ferrous sulphate solution every day. Test results obtained in this way on pure solutions containing iron, manganese, and chromium, and on chromium steels, are excellent for both the manganese and chromium. If tungsten or molybdenum is also present, a carbide of chromium insoluble in sulphuric acid, may be left, which requires fusion with sodium carbonate. If vanadium is present, the manganese cannot be determined by sodium arsenite; in this case the bismuthate or Ford's method may be used. A. G. L.

Estimation of Chromium and Manganese. A. Kleine. (*Chem. Zeit. Rep.*, 1905, xxix., 380.)—Five grams of steel shavings are dissolved in 500 c.c. HCl (1·12) by the aid of heat, the solution is heated to boiling, and all subchlorides converted into perchlorides by adding 3 c.c. of HNO_3 (1·4) drop by drop. The solution is then

evaporated to a syrup, and the iron extracted by shaking with ether. The iron-free solution is evaporated to dryness, the residue taken up by 10 c.c. sulphuric acid (1 : 10), the solution diluted, treated with ammonium persulphate (60 grams per litre), and boiled for fifteen to twenty minutes. The precipitated manganese peroxide is filtered off and washed. The chromium is estimated in the filtrate by adding excess of iron sulphate solution (50 grams $FeSO_4$ in 800 c.c. $H_2O + 200$ c.c. H_2SO_4), and the excess titrated with standard permanganate solution. The iron titre of the permanganate $\times 0.31$ gives the chromium titre. The washed manganese precipitate is then transferred to the precipitation flask, 10 c.c. of sulphuric acid added, and sufficient oxalic acid solution run in to completely dissolve the precipitate. The excess of oxalic acid, after dilution with 200 to 300 c.c. of hot water, is estimated by permanganate. To obtain the manganese titre of the permanganate the iron titre must be multiplied by 0.501 (according to Ledebur), and not by the older value 0.491.

For crude iron and difficultly soluble chromium steel 5 grams of the metal should be dissolved in 50 c.c. of $HCl + 5$ c.c. HNO_3; the solution is then diluted, filtered from silica, evaporated and shaken up with ether, and treated as above. For steel with a high percentage of chromium the filtrate from the manganese precipitate should be made up to 500 c.c. and the chromium estimated in an aliquot part.   E. K. H.

The Ford-Williams Method for High-grade Manganese Ores. J. James Skinner. (*Chem. Engineer*, 1905, ii., 279.)—0.5 gram of the ore is digested with 20 c.c. hydrochloric acid until the residue is white, after which the solution is evaporated down to a syrup. It is then boiled with 110 c.c. nitric acid until the red fumes are almost wholly driven off, when half a teaspoonful of fine asbestos fibre is added carefully, and boiling continued for one minute more, when 8 grams potassium chlorate are added, and the whole boiled for another ten minutes. The precipitate is then filtered off, as usual, on an asbestos filter. Precipitate and filter are then dropped into a beaker containing 0.750 gram of pure oxalic acid, 50 c.c. of dilute sulphuric acid, and 150 c.c. of warm water. After gently warming until the whole of the manganese dioxide has dissolved, the liquid is titrated with standard potassium permanganate, with which another portion of 0.750 gram oxalic acid is also titrated, the difference corresponding to the manganese.

For ores containing manganese in a form insoluble in hydrochloric acid, the insoluble portion is filtered off, treated with hydrofluoric and sulphuric acids, and, after evaporating off the hydrofluoric acid, dissolved in hydrochloric acid and added to the main solution.   A. G. L.

A New Reagent for Potassium. E. P. Alvarez. (*Gazz. Chim. Ital.*, 1905, xxxv., 463; through *Chem. Zeit. Rep.*, 1905, xxix., 404, 405.)—The reagent consists of a saturated (5 per cent.) solution of amido-naphthol sulphonic acid,

$$C_{10}H_5 \diagdown \begin{array}{l} NH_2(1) \\ OH(2) \\ SO_3Na(6). \end{array}$$
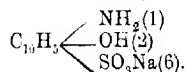
It should be prepared with recently-boiled cold water shortly before it is required for

use. It can only be kept in black bottles from which the air is carefully excluded. The precipitate of potassium amido-naphthol-sulphonate is given by all potassium salts, including the iodide, provided the solution be neutral. Ammonium salts, and magnesium salts in the presence of ammonium chloride, are not precipitated by the reagent. Solutions of potassium salts of the strength of 5 to 10 per cent. give the reaction almost immediately; those containing from 3 to 5 per cent. do not give a precipitate until after ten minutes; and those containing 1 per cent. not until after several hours. C. A. M.

Colorimetric Estimation of Selenium. J. E. Clenell. (*Chem. Zeit. Rep.*, 1905, xxix., 392.)—The selenium must be brought into solution as selenite or selenate; this can be effected by treatment with concentrated nitric acid and subsequent addition of hydrochloric acid; the free chlorine must then be driven off. A white precipitate in the solution is of no account, and may, if necessary, be produced in the comparison test by precipitating zinc chloride with potassium ferrocyanide. The solution is heated to boiling, and a few c.c. of a 5 per cent. solution of sodium bisulphite added. In case of cyanide solutions, 100 c.c. boiled with 10 c.c. HCl for five minutes give the precipitate of selenium without any addition of sulphite. The finely divided selenium remains some time in suspension, and the tint it gives is compared with that of known amounts of a standard solution prepared by shaking 0·1 gram selenium with strong bromine water until dissolved, adding bicarbonate gradually until a colourless solution is obtained, and making up to a litre. The standard tests are boiled with 5 to 10 c.c. of sodium bisulphite, as before.

The only element which interferes with this process is copper, which with potassium ferrocyanide gives a colour similar to that of the suspended selenium.

The estimation takes about fifteen minutes. E. K. H.

The Use of the Rotating Anode and Mercury Cathode in Electro-analysis. Second Paper. Lily G. Kollock and Edgar F. Smith. (*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1527.)—Continuing their work, the authors have applied the rotating anode and mercury cathode to metals other than those dealt with in their first paper (ANALYST, 1905, xxx., 413). The apparatus used was the same as before, except that the weight of mercury used was increased to 60 or 70 grams. For *cadmium*, good results were obtained by electrolysing 5 c.c. of solution containing 0·9480 gram of cadmium as sulphate, and ¼ c.c. of concentrate sulphuric acid for fifteen minutes, with a current of 3·5 ampères and 10 to 7 volts. For *tin*, the best results were obtained with 10 c.c. of solution containing 0·8212 gram of tin as stannous sulphate, and 0·5 c.c. of sulphuric acid, using a current of 5 ampère and 5 to 4 volts for eight minutes. For *silver*, the best results were obtained with 5 c.c. of solution containing 0·2240 gram of silver as nitrate, and ⅛ c.c. of nitric acid, using a current of 4·5 to 3 ampères at 6·5 to 6 volts for five minutes, and giving the anode the high speed of 1,200 revolutions per minute. No nitric acid was reduced and hence no ammonium was found in the amalgam. For *mercury*, 5 c.c. of solution containing 0·3575 gram of mercury as mercurous nitrate and 0·02 c.c. of nitric acid gave the best results with a current of 3 ampères and 7 to 5 volts for three minutes;

diluting the liquid to 25 c.c. increased the time necessary to eight minutes. For *bismuth*, the best conditions were: Volume, 12 c.c.; bismuth, as sulphate, 0·2273 gram; 0·5 c.c. of sulphuric or nitric acid; current, 3 or 4 ampères at 5 to 5·75 volts; time, fifteen minutes for sulphuric, and twelve minutes for nitric, acid solutions. The platinum wire used as anode should be very smooth, in order that the bismuth peroxide at first deposited on it may be readily dissolved.

Experiments to determine halogens in metallic haloid salts by using a silver-coated rotating anode proved unsuccessful, some of the deposit always becoming detached. It was found possible, however, to determine the metal in such salts, the free halogen being suppressed by adding 10 c.c. of toluene to the liquid. The most favourable conditions found are summarized in the following table:

Metal.	Amount taken (gram).	Volume of Liquid (c.c.).	Ampères.	Volts.	Time (minutes).	Maximum Error (gram).
As Chloride :						
Cobalt ...	0·1050	5	2 to 4	5	7	± 0·0002
Gold ...	0·1200	5	2 to 3	10	5	− 0·0002
Ferric ...	0·1030	5	2 to 4	9	12	− 0·0005
Mercuric ...	0·2525	5	1 to 3	10 to 7·5	10	− 0·0001
Stannous ..	0·0800	5	2 to 3	7 to 6	10	+ 0·0006
Ditto ...	0·1600	10	2 to 3	7 to 6	15	− 0·0005
As Bromide :						
Cadmium ...	0·2212	5	2	5	10	+ 0·0003

The anode was not attacked in these experiments; xylene may be used instead of toluene, which is probably converted into a mixture of *o*- and *p*- chlortoluene.

It was also found possible to separate iron quantitatively in this way from uranium, aluminium, thorium, lanthanum, praseodymium, neodymium, cerium, and zirconium. The metals were used in the form of sulphates. The quantity of iron present was 0·12 to 0·18 gram, and of the sulphate of the other metal 0·1 to 0·5 gram. The volume of the liquid varied from 6 to 10 c.c., the quantity of free sulphuric acid from 0 to $\frac{1}{5}$ c.c., the current from 2 to 5 ampères at 9 to 5 volts, and the time from fifteen to twenty-five minutes. The maximum error in twenty-nine experiments was − 0·0008 gram iron.　　　　　　　　　　　　　　　　A. G. L.

Estimation of Vanadium. W. Heike. (*Chem. Zeit. Rep.*, 1905, xxix., 392.) —A comparison of four methods for purposes of technical iron works:

1. The ore is fused with sodium potassium carbonate, extracted with hot water, filtered, the filtrate acidified with H_2SO_4, the vanadic acid reduced to vanadic oxide with zinc, and the amount estimated by titration with standard permanganate. The vanadium titre = iron titre × 0·035.

2. The ore is dissolved, the iron extracted by shaking out with ether, the solution treated with H_2O_2, and the vanadium estimated by comparing the tint (yellow-red) with that of known vanadic solutions.

3. Ledebur dissolves the iron, etc., in diluted hydrochloric acid, separates the chromium and vanadium from iron and manganese by neutralizing with the barium carbonate, fuses the residue with sodium carbonate and nitre, and extracts the chromates and vanadates with hot water. The solution is then reduced with alcohol and hydrochloric acid, the chromium precipitated with ammonium phosphate and ammonia, the vanadium transformed by ammonium sulphate into the sulphide, and precipitated as sulphide with acetic acid. On heating vanadic acid is obtained.

4. Campagne extracts the iron with ether (as in 2), reduces the vanadic acid by evaporation with hydrochloric acid to V_2O_4, displaces the hydrochloric acid by sulphuric acid, warms to 60° to 70°, dilutes to 300 c.c., and titrates with potassium permanganate. The vanadium titre here = iron titre $\times$ 0·914.

The author obtained the following figures:

	I.	II.	III.	IV.
Iron ore	0·07		---	0·11
Fresh slag	1·40		---	1·46
Gray crude iron with 0·14 Cr.	0·15		0·21	0·21
Steel with 0·02 Cr.	--	0·21	0·27	0·54
Steel	--	0·42	0·54	0·54

He concludes by stating that Campagne's method is very suitable for estimation of ferrovanadium, especially where chromium is not present in large quantity, otherwise Ledebur's method is to be preferred.　　　　　　　　E. K. H.

Moisture and Water of Constitution in Bauxite. H. Lienau. (*Chem. Zeit.*, 1905, xxix., 1280.)—The view has often been expressed that the moisture in bauxites must be estimated by drying in the desiccator and not in the oven, as the water of hydration begins to come off even at 100° C.

The author performed experiments to test this view. The powdered bauxite was wetted with 14 to 15 per cent. of distilled water, and five samples of 10 to 15 grams were placed in stoppered weighing bottles and dried for ten hours at 100°, allowed to stand overnight in a desiccator, and weighed. They were then dried for ten hours at 110°, allowed to stand as before, and again weighed. This was repeated for temperatures of 150° and 200°. It might then be supposed that a characteristic gap would occur between the loss of the moisture and that of the water of constitution. As a matter of fact, for most kinds of bauxite no such gap could be distinguished, but the loss of water was continuous with rise of temperature, until the whole of the water of hydration was evolved, and a constant weight obtained at bright red heat.

The term "bauxite" includes materials of very different constitution, but the French varieties at least (on which the experiments were performed) can be divided into two great classes: (1) The diaspore group, containing alumina monohydrate, and (2) the true bauxite group, containing alumina dihydrate. The author gives figures for both classes, for which reference must be made to the original. The conclusions arrived at may be summarized as follows:

For the monohydrate group, which forms about 90 per cent. of commercial bauxites, the weight alters evenly up to 200° C., but so slowly that the loss in weight

between 100° and 200° is only 0·09 per cent. It is not possible to say at what point the combined water begins to be given off, but it is probably fair to assume that there is no more adherent moisture at 110°, as the loss between 100° and 110° = 0·02, whilst loss between 110° and 150° = 0·03 per cent. This is further made more likely by the behaviour of the dihydrate group.

One specimen of this class from Maussane, near Arles, showed a distinct gap between the two kinds of water, the weight remaining constant between 110° and 150°. The author considers this characteristic, and thinks that in these bauxites the water of hydration only begins to come off after all the adherent moisture has been driven off.

The author concludes that in all bauxites the total loss in weight up to 110° C. may be taken as adherent moisture.   E. K. H.

Volumetric Estimation of Sulphates in Presence of Thiosulphates, etc.
O. Huber. (*Chem. Zeit.*, 1905, xxix., 1227.)—The author investigated the process originally brought forward by Müller and Dürkes for the volumetric estimation of sulphates with benzidin hydrochloride, and extended it to the estimation of sulphates when thiosulphates, sulphites, and sulphides were also present. The only modification made was the substitution of caustic potash for caustic soda. The author gives figures which show an error of about 2 per cent. in value for total sulphate, and states that this process is inaccurate for the following reasons :—The use of so many titrations, the errors of which may all lie in the same direction, but chiefly, in the author's opinion, through the defects of the benzidin process itself.. He concludes that the chief factor in rendering the process inexact is the great solubility of the benzidin sulphate, whilst the absorption phenomena noted by Müller and Dürkes are less important.

For further details and the figures given reference must be made to the original.
                                                                         E. K. H.

Estimation of Sulphuric Acid by Means of Barium Chloride in the Presence of Disturbing Substances. G. Lunge and R. Stierlin. (*Zeit. angew. Chem.*, xviii., 1921.)—The authors come to the conclusion that the precipitation of barium chloride as sulphate is by no means complete in the presence of many salts. Thus, if sodium, potassium, or ammonium salts are present, part of the barium sulphate is held in solution. Zinc and copper compounds may, however, be present without disturbing the reaction in any way. This undesirable influence is negligible, however, if the precautions suggested by Lunge (*Zeit. anal. Chem.*, 1881, vol. xix., p. 149) are adhered to.   H. D. L.

The Determination of Nitrous and Nitric Acids. J. Meisenheimer and F. Heim. (*Berichte*, 1905, xxxviii., 3834-3837.)—This method, which is claimed to give rapid and accurate results in the simultaneous determination of nitrous and nitric acids, is based upon the following reactions :

$$HNO_2 + HI = NO + I + H_2O$$
$$HNO_3 + 3FeCl_2 + 3HCl = NO + 3FeCl_3 + 2H_2O.$$
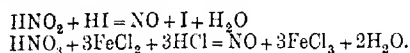
The slightly alkaline solution of the substance (0·1 to 0·2 gram of nitrite) is placed in a round-bottomed 50 c.c. flask closed by an indiarubber stopper with three openings. One of these receives a thistle funnel with a stop cock ; the second holds a delivery-tube, the outside portion of which dips into a trough containing a 12 per cent. solution of sodium hydroxide ; whilst the third receives a tube for the introduction of a current of carbon dioxide. The air is first swept out of the flask by means of this gas for about ten minutes, after which a eudiometer filled with sodium hydroxide solution is fixed above the delivery tube, and then by means of the funnel, the tube of which has previously been filled with water up to the stop-cock, there are intro-duced 10 to 15 c.c. of a 5 per cent. solution of potassium iodide, followed by the same quantity of dilute hydrochloric acid, added little by little. When the evolution of gas slackens, the contents of the flask are heated to incipient boiling, and the last portions of nitric oxide expelled by means of a current of carbon dioxide. The amount of gas contained in the eudiometer is then measured in the usual manner.

For the determination of nitrates in the residue, from 10 to 20 c.c. of a con-centrated solution of ferrous chloride, acidified with hydrochloric acid, are introduced into the flask, and the gas collected as described in Spiegel's modification of the method of Schulze and Tiemann (*Berichte*, 1890, xxiii., 1361). C. A. M.

The Determination of Nitrous Acid. F. Raschig. (*Berichte*, 1905, xxxviii., 3911-3914.)—The method described by Meisenheimer and Heim (see preceding abstract) has been applied by the author to the determination of nitrous acid in solu-tions containing also hydroxylamine, but instead of measuring the nitric oxide in a eudiometer he titrates the separated iodine, a determination being made in five to ten minutes. The solution (about 100 c.c.) is placed in a 200 c.c. conical flask, into which are then introduced 5 to 10 c.c. of a 10 per cent. solution of potassium iodide. A current of carbon dioxide is now admitted through a tube passing nearly to the bottom of the flask, and after two or three minutes about 1 c.c. of $\frac{N}{10}$ sulphuric acid is poured down the side of this tube, and the mixture allowed to stand for two minutes, and then titrated with the standard thiosulphate solution, which is also made to run down the side of the tube. The bubbles of gas evolved cause the liquids to mix, and thus the flask need not be shaken, which would cause oxidation of the escaping nitric oxide. In the author's opinion nitrosyl iodide (NOI) is first formed on adding the acid, and this is then decomposed, so that it is necessary to wait for a time before titrating the solution ; otherwise the results will be too high. The author prefers the sul-phanilic acid and permanganate methods where possible, but they cannot be employed in the presence of hydroxylamine As regards the permanganate method, he uses an excess of at least 20 per cent. of $\frac{N}{10}$ permanganate solution, into which the solution under examination is poured. The mixture is acidified, if required, and allowed to stand for two minutes, when the whole of the nitrous acid will have been oxidized to nitric acid. The liquid is then treated with 5 c.c. of a 10 per cent. solution of potassium iodide, which dissolves any manganese peroxide, and the liberated iodine titrated with standard thiosulphate solution. C. A. M.

The Reactions of the three Phosphoric Acids.   C. Arnold and G. Werner.

(*Chem. Zeit.*, 1905, xxix., 1326, 1327.)—The authors have tested all the reactions described in chemical text-books as means of distinguishing between the three phosphoric acids, and have found that in nearly every instance they are unreliable. They have therefore made a new series of tests with the alkali salts of the acids, and the principal results obtained are summarized in the following table:

REAGENT.	ORTHOPHOSPHORIC ACID.	PYROPHOSPHORIC ACID.	METAPHOSPHORIC ACID.
Barium chloride ...	White ppt. Insol. in excess of alkali phosphate. Sol. in acetic acid. Sol. in NH_4Cl.	White ppt. Insol. in excess of alkali pyrophosphate. Insol. in acetic acid. Insol. in NH_4Cl.	White ppt. Sol. in excess of alkali metaphosphate. Insol. in acetic acid. Insol. in NH_4Cl.
Calcium chloride ...	White ppt. Insol. in excess of phosphate. Sol. in acetic acid. Sol. in much NH_4Cl.	White ppt. Scarcely sol. in excess of pyrophosphate. Sol. in acetic acid. Insol. in NH_4Cl.	White ppt. Sol. in excess of metaphosphate. Insol. in acetic acid. Insol. in NH_4Cl.
Magnesium sulphate	White flocculent ppt. Insol. in excess of phosphate and in excess of $MgSO_4$. Sol. in acetic acid.	White ppt. Sol. in excess of pyrophosphate. Sol. in acetic acid. Insol. in NH_4Cl.	White ppt. Sol. in excess of metaphosphate and in excess of $MgSO_4$. Insol. in acetic acid.
Magnesia mixture ...	White crystalline ppt. Insol. in excess of phosphate and of reagent. Readily sol. in acetic acid.	White ppt. Sol. in excess of pyrophosphate and of reagent. Sol. in acetic acid. In very dilute solutions ppt. only formed after heating.	White ppt. Sol. in excess of metaphosphate. Insol. in excess of reagent and in acetic acid.
Aluminium sulphate	White ppt. Sol. in excess of phosphate and in acetic acid.	White ppt. Sol. in excess of pyrophosphate. Insol. in acetic acid.	White ppt. Sol. in excess of metaphosphate. Insol. in acetic acid.
Chromium sulphate	Greenish ppt. Insol. in excess of phosphate. Sol. in acetic acid.	Dirty-white ppt. Insol. in excess of pyrophosphate and in acetic acid.	Dirty white ppt. Sol. in excess of metaphosphate. Insol. in acetic acid.
Ferrous sulphate ...	Green ppt. Insol. in excess of phosphate.	White ppt. Sol. in excess of pyrophosphate.	—
Ferric chloride ...	Yellow ppt. Insol. in excess of phosphate. Sol. in HCl.	White ppt. Hardly sol. in excess of pyrophosphate. Sol. in HCl.	White ppt. Sol. in excess of metaphosphate and in much HCl.
Manganese sulphate	White ppt. Insol. in excess of phosphate. Presence of much pyrophosphate prevents ppt.	White ppt. Hardly sol. in excess of pyrophosphate.	White ppt. Readily sol. in excess of metaphosphate.
Zinc sulphate ...	White ppt. Insol. in excess of phosphate. Sol. in NH_3 and in acetic acid. Metaphosphate does not prevent ppt.	White ppt. Sol. in excess of pyrophosphate. Sol. in NH_3. Insol. in acetic acid. Metaphosphate does not prevent ppt.	
Cobalt nitrate ...	Blue ppt. Insol. in excess of phosphate. Sol. in acetic acid.	Rose ppt. Sol. in excess of pyrophosphate. Insol. in acetic acid.	Rose ppt. Sol. in excess of metaphosphate. Insol. in acetic acid.
Nickel sulphate ...	Greenish-white ppt. Insol. in excess of phosphate. Sol. in acetic acid.	Greenish-white ppt. Sol. in excess of pyrophosphate. Sol. in acetic acid.	

REAGENT.	ORTHOPHOSPHORIC ACID.	PYROPHOSPHORIC ACID.	METAPHOSPHORIC ACID.
Uranium nitrate $(UO_2)(NO_3)_2$	Yellow ppt. Insol. in excess of phosphate.	White ppt. Sol. in excess of pyrophosphate.	White ppt. Sol. in excess of metaphosphate.
Silver nitrate ...	Yellow ppt. Insol. in excess of phosphate. Sol. in HNO_3 and NH_3.	White ppt. Insol. in excess of pyrophosphate. Sol. in HNO_3 and NH_3.	White ppt. Sol. in excess of metaphosphate. Sol. in HNO_3 and NH_3.
Lead acetate ...	White ppt. Insol. in excess of phosphate. Sol. in KOH and HNO_3. Sol. in hot dilute HCl. Sol. in much tartaric acid.	White ppt. Sol. in excess of pyrophosphate and in KOH, HNO_3, hot dilute HCl, and much tartaric acid.	White ppt. Sol. in excess of metaphosphate, in KOH, HNO_3, and hot dilute HCl. Insol. in tartaric acid.
Mercurous nitrate ...	Yellowish-white ppt. Insol. in excess of phosphate. Sol. in HNO_3.	White ppt. Sol. in excess of pyrophosphate. Sol. in very much HNO_3.	White ppt. Sol. in excess of metaphosphate. Hardly sol. in HNO_3.
Mercuric chloride ...	Immediate yellow ppt. In concentrated solution yellow turbidity, and deep violet-red ppt. after some hours.	In concentrated solution red fluorescent turbidity after a few minutes. Then reddish-brown ppt.	
Alkaline bismuth solution			White ppt. (also in presence of ortho- and pyrophosphate). Sol. in excess of metaphosphate.
Copper sulphate ..	Greenish-blue ppt. Insol. in excess of phosphate. Sol. in NH_3 and acetic acid.	Bluish-white ppt. Sol. in excess of pyrophosphate and NH_3. Insol. in acetic acid.	
Cadmium sulphate ...	White ppt. Insol. in excess of phosphate. Sol. in NH_3 and in acetic acid.	White ppt. Insol. in excess of pyrophosphate. Sol. in NH_3. Insol. in acetic acid.	White ppt. Sol. in excess of metaphosphate. Sol. in NH_3. Insol. in acetic acid.

For the detection of metaphosphoric acid in the presence of the other two acids, the authors consider the reactions with alkaline bismuth solution (vide supra) and with cobaltamine solution particularly suitable. The latter reagent is prepared by mixing equal parts by volume of solutions of a cobaltous salt and an ammonium salt, adding a few drops of ammonium hydroxide, and shaking the solution until it becomes perceptibly brown. It gives a brownish-yellow precipitate with a metaphosphate even when only present in traces in ortho- and pyrophosphates. Pyrophosphoric acid in the presence of the other acids is best identified by its behaviour with copper sulphate and zinc sulphate in acetic acid solution.   C. A. M.

Estimation of Phosphoric Acid in Thomas Meal, Bone Meal, etc. O. Bottcher. (*Chem. Zeit.*, 1905, xxix., 1293.)—1. *Estimation of Citric Acid Soluble Phosphate in Thomas Meal.*—The author maintains, against various critics, that, as agreed upon by the Union of Agricultural Research Stations (in Germany), the phosphate can be directly precipitated without error with magnesia mixture containing citrate, without previous separation of silica, by evaporation with hydrochloric acid, even in cases where a high percentage of silica is shown by a preliminary test. The process gives accurate results so long as the essential condition is observed that all

the operations are carried through successively without interruption. If the citric acid extracts, or the precipitations with citrate-containing magnesia mixture, are allowed to stand for hours, considerable quantities of silica may come down with the phosphate precipitate and cause a too high result. The separation of silica is always indicated by the bad filtering property of the solution, and this serves as a valuable check on the purity of the precipitate. The author has carried out analyses on over 800 samples of Thomas meal in the last year, and in no case encountered this complication.

The author gives figures which show very exact agreement between the results obtained by this direct estimation and those obtained by first separating the silica.

2. *Estimation of Total Phosphate in Thomas Meal, Bone Meal, etc.*—The author again defends the process prescribed by the Union of Agricultural Research Stations: (1) Against the criticism of V. Schenke, who, finding 0·3 to 0·4 too little phosphoric acid by this method, as against the molybdate method, recommended approximately neutralizing the strongly acid solution before precipitation; and (2) against those analysts who consider that extraction with aqua regia gives less reliable results than extraction with sulphuric acid, partly because the compensation in the aqua regia solution varies with the kind and amount of bases present, and partly because all the organic acids are not decomposed by the aqua regia, so that the calcium salts of these acids accompany the precipitate, being insoluble in ammonium citrate solution. the author gives figures of comparative analyses which show that the modifications suggested by these criticisms make no appreciable difference, and that the Union process is quite satisfactory.   E. K. H.

The Determination of Tellurous and Telluric Acids. A. Berg. (*Bull. Soc. Chim.*, 1905, xxxiii., 1310-1312.)—The author's method depends upon the facts that these acids are readily converted into tellurium chloride by the action of gaseous hydrochloric acid, and that the chloride formed can easily be sublimed. The apparatus required is a combustion tube of hard glass, the front part of which is bent at a right angle and drawn out to a fine opening, which is directed downwards and connected with two small U-tubes containing water. The tube is placed in a combustion furnace and its other end connected with an apparatus giving a current of hydro chloric acid gas. The substance to be analysed is placed in a porcelain boat which is introduced into the tube. The air is swept out by means of a moderate current of the gas, and the tube rapidly heated to a temperature below red heat. The tellurium chloride which sublimes on the tube is driven forward by the application of a Bunsen burner. If the process is properly carried out no white fumes should be seen in the absorption tubes, and the liquid in the second tube should remain colourless. When the reaction is complete, the yellow solution of tellurium chloride is transferred to a weighed porcelain crucible, and after the addition of 5 c.c. of nitric acid evaporated slowly on a sand bath. The presence of this nitric acid prevents the volatilization of the tellurium chloride. When the evaporation has proceeded to dryness, the residue must be cautiously heated so as to decompose all the tellurium nitrate without fusing the tellurous acid, part of which would then escape with the nitrous vapours. With a little care this can readily be done. The residue is then weighed as tellurous anhydride. When metallic tellurites or tellurates are to be

analysed, the residue of chloride left in the boat can be weighed directly. In a test experiment 58·66 per cent. of tellurous anhydride was found as compared with the theoretical 58·26 per cent. A barium tellurite containing, according to theory, 60·94 per cent. of tellurous anhydride was found to contain 60·28 per cent. The method is obviously only applicable in the absence of compounds of substances, such as mercury or chromic acid, which yield readily volatile compounds under these conditions. C. A. M.

The Volumetric Estimation of Cyanates. A. C. Cumming and Orme Masson. (*Chem. News*, 1906, vol. 93, pp. 5 and 17.)—A known volume of the cyanate solution is first of all titrated in the cold with standard acid, using congo-red or methyl orange as indicator; the first end-point obtained should be taken. This gives the quantity of carbonate present, carbonate being always contained in cyanate solutions. An excess of the acid is then added, and the liquid boiled for a few minutes, when the cyanate is hydrolysed according to the equation :

$$KCNO + 2HCl + H_2O = KCl + NH_4Cl + CO_2.$$
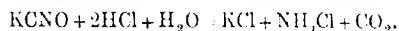
The liquid is then cooled and the excess of acid titrated back with standard alkali, the quantity consumed being calculated to cyanate. As a further check the ammonia formed may be determined by boiling the liquid for some time with an excess of standard alkali and titrating back. The method appears to give good results. If cyanide is present it is determined by means of standard silver nitrate, and allowed for in calculating the results. Ferrocyanide in small quantities does not interfere. The solutions used should be rather dilute, as otherwise the acid might act on the cyanate in the cold, and render the first end-point indefinite.

A. G. L.

Determination of Cyanides in Crude Coal-Gas. (*Chem. Trade Jour.*, 1906, xxxviii., 72, 73.)—In the proposed method, the cyanides are absorbed by freshly precipitated ferrous hydroxide suspended in sodium hydroxide solution. This is prepared by dissolving 4 grams of crystallized ferrous sulphate in 500 c.c. of water at a temperature of 80° C., adding 4 grams of sodium hydroxide dissolved in water also at 80° C., and boiling the mixture. The precipitate is allowed to settle, washed by decantation, and then mixed with 250 c.c. of 4 per cent. sodium hydroxide solution. Water is finally added to make the volume up to about 800 c.c., and the mixture transformed to an absorption apparatus, which consists of a tall glass jar closed at the top with a caoutchouc stopper perforated by two holes. The central one of these carries a length of half-inch solid-drawn nickel tubing reaching to the bottom of the cylinder, and upon which are brazed twelve perforated nickel cones. The liquid should fill the cylinder up to the base of the topmost cone. Ten cubic feet of gas are usually sufficient for one test, and this volume is passed through the apparatus at the rate of 5 cubic feet per hour. At the end of the operation the contents of the cylinder are washed out into a litre flask and diluted to the mark. A known volume of this solution is then boiled to expel ammonia, then treated with sodium plumbate to remove sulphide (in this operation free sodium hydroxide

must be present), made up to the correct volume, and the amount of ferrocyanide formed determined in it.　　　　　　　　　　　　　　　　　　　　　W. P. S.

Purification of Hydrochloric Acid from Arsenic. (German Patent, *Apoth. Zeit.*, xx., 932; through *Pharm. Jour.*, 1905, lxxv., 910.)—Vanadous salts rapidly reduce arsenious chloride to metallic arsenic, which separates from the solution in the form of minute particles, or as a flocculent precipitate which can easily be filtered off. On a large scale the hydrochloric acid gas is passed through earthenware vessels containing a concentrated solution of vanadous chloride, which retains the arsenic, and is simultaneously oxidized to vanadic chloride. The latter can be reconverted into vanadous chloride.　　　　　　　　　　　　　　W. P. S.

A New Method of Determining the Strength of Iodine Solutions. Sigmund Metzl. (*Zeits. anorg. Chem.*, 1906, xlii., 156.)—The author proposes to standardize iodine solutions used for titrating antimony compounds by means of tartar emetic, either as the crystallized salt, $KSbO(C_4H_4O_6) + H_2O$, or in the anhydrous condition. The tartar emetic is dissolved in hot water containing tartaric acid, a trace of solid phenolphthalein and an excess of sodium carbonate are added, after which CO_2 is led through the liquid until the red colour is destroyed. The titration is then made as usual with the iodine solution to be standardized. The results obtained are in good agreement with those obtained by standardizing a thiosulphate solution with potassium bichromate in the usual way, and titrating the iodine against the thiosulphate. The author also recommends the use of potassium hydrogen iodate, which reacts with potassium iodide as follows in acid solution :

$$KH(IO_3)_2 + 10KI + 11HCl = 6I_2 + KCl + 6H_2O$$

and in neutral solution according to the equation :

$$6KH(IO_3)_2 + 5KI = 3I_2 + 11KIO_3 + 3H_2O,$$
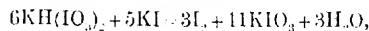
whilst its purity can be easily determined by titration with alkali.　　　　A. G. L.

Tests and Reactions of Hydrogen Peroxide. C. Schmatolla. (*Pharm. Zeit.*, 1905, l., 611; through *Pharm. Jour.*, 1905, lxxv., 910.)—Ten c.c. of hydrogen peroxide should not require more than 0·25 c.c. of $\frac{N}{10}$ alkali for neutralization, using Congo red as an indicator. The presence of hydrochloric acid is very objectionable in samples intended for medicinal use, and hydrogen peroxide containing more than 0·01 per cent. of chlorine should be rejected. To determine this impurity, 10 c.c. of the sample are treated with 25 drops of dilute sulphuric acid, 0·5 gram of ferrous sulphate, and 5 c.c. of $\frac{N}{10}$ silver nitrate solution. The silver is then titrated back with $\frac{N}{10}$ thiocyanate solution.

The following test will detect hydrogen peroxide in a dilution of 1 : 1,000,000 : 200 c.c. of the solution to be tested are acidified with a few drops of dilute sulphuric acid, and about the same quantity of a 1 per cent. cobalt nitrate solution is added. On then adding potassium hydroxide solution drop by drop, a sharp brown colour-reaction is produced if hydrogen peroxide be present.　　　　　　　　W. P. S.

A Substitute for Hydrogen Sulphide. J. Ducommun. (*Chem. Zeit. Rep.*, 1905, xxix., 379.)—The acidified solution of the metal or metallic salt is treated with 2 to 5 c.c. of formalin solution, and then with a moderately concentrated solution of pure sodium sulphide. If a metal of the arsenic-tin group be present, the corresponding sulphide is at once precipitated. On adding alkali to the filtrate, the precipitate of the iron group is obtained. The addition of the formalin prevents any separation of sulphur. E. K. H.

Determination of Oil in Paraffin-Scale. L. Neustadtl. (*Chem. Zeit.*, 1906, xxx., 38.)—In the method proposed, advantage is taken of the insolubility of paraffin in acetone at a temperature of −15° C., whilst the oil present is completely soluble. One gram of the finely-divided paraffin-scale is mixed with 10 c.c. of acetone, and allowed to stand for two hours at the ordinary temperature, with occasional shaking. The mixture is then cooled to −15° C., and the solid paraffin collected on a small plug of cotton-wool contained in a filter-tube. The latter is surrounded by a funnel, and the space between the two filled with a freezing mixture. After washing the filter and its contents with acetone cooled to −15° C., the filtrate and washings are evaporated, the residue is dried at 100° C. and weighed. The results obtained are, as was to be expected, somewhat higher than those yielded by the older methods in which the oil was pressed out. W. P. S.

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REVIEW.

SELECT METHODS IN FOOD ANALYSIS. By Drs. LEFFMAN and BEAM. (London: Rebman. Price 11s. net.)

Since the publication in 1901 of this very useful handbook considerable additions have been made to our knowledge of food chemistry, and many new processes have been devised. This progress, to which American chemists have contributed a very full share, has necessitated a revision of the work and the insertion of much new matter. Among the more important additions are descriptions of useful distillation and extraction processes; new methods for the detection of natural colours used as substitutes for fruit colours; improvements in the detection and estimation of formaldehyde, boric acid, and other preservatives; and some new information in connection with the analytical chemistry of butter, oleo-margarine, and other fats. The arrangement of the book leaves nothing to be desired, and although the descriptions of analytical processes are invariably brief, in very few cases has compression been secured at the expense of clearness. The estimation of minute traces of arsenic in food products is a matter with which American chemists are perhaps not quite so intimately acquainted as their English colleagues, and the section devoted to this subject is capable of being improved.

On p. 62 the operator is told to use 3 grams of zinc in the Marsh-Berzelius flask, and to allow the action to proceed for one hour after the addition of the material to be

tested. It is not quite clear how a sufficient supply of gas is to be obtained by the employment of so small an amount of metal in a test which, according to the authors' instructions, is to last for rather more than one and a half hours. Nothing, moreover, is said to warn the analyst against the use of "insensitive" zinc. On p. 91 the size of the pepper-starch granules is curiously said to vary from 0 to 5·5 microns. Mention is made of the use of cocoanut oil as a direct or indirect butter adulterant, but it is to be regretted that the authors do not give more detailed and definite information as to the methods to be employed for its detection. The illustrations are as a rule good, the plate showing the microscopical appearance of certain of the starches being one of the least satisfactory. To the English eye such words as *sirup* and *analogs* have a strange appearance, but the spelling may perhaps be defended on the ground of simplicity, and at least does no violence to the principles of etymological science. The same cannot, however, be said for the word *levulose*.

The work is described in the authors' preface as being intended "for the practical worker in the detection of food adulteration," and all such will welcome it as one of the best contributions to this important subject which has yet appeared.

A. C. C.

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INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

ANNUAL MEETING.

THE twenty-eighth Annual General Meeting of the Institute of Chemistry of Great Britain and Ireland was held at 30, Bloomsbury Square, on Thursday, March 1, Mr. David Howard, the retiring President, in the chair.

The accounts for 1905 having been submitted by the HON. TREASURER (Mr. A. Gordon Salamon), and duly received, Dr. JOHN A. VOELCKER moved the adoption of the Annual Report. He congratulated the Council on their work during the past year, and he specially alluded to the steps they had taken to protect the interests of professional chemists. Mr. ARTHUR E. EKINS seconded, and the Report was formally received and adopted.

Scrutineers having been appointed to count the votes sent in for the election of the officers and members of Council, and ballot having been taken for the election of censors, the meeting proceeded to select the honorary auditors, and Messrs. Robert E. Alison, W. T. Burgess, and P. A. E. Richards were appointed.

The PRESIDENT then delivered his address. After referring to the progress made by the Institute during his term of office as President, he dealt more particularly with the history of the third and last year.

While the roll of Fellows and Associates has steadily increased, he noted with regret the death of some of the original Fellows, and he mentioned especially John Lloyd Bullock, largely to whose incentive was due the foundation of the Royal College of Chemistry and the invitation to Hofmann to come to London. How much that meant to not a few, including several past Presidents of the Institute, it would take long to tell.

The Institute was examining over one hundred candidates yearly, and arrangements would be made from time to time for examinations in the colonies.

Mr. HOWARD alluded to the improvement in the financial position of the Institute, and to the steady growth of the library. He paid a high tribute to the services of Professor Adrian J. Brown, who had held the appointment of Examiner to the Institute in Biological Chemistry since 1901, and stated that, as his term of office had expired, the Council had selected Dr. Arthur Harden, of the Lister Institute, as his successor.

He also referred to the new examinations in technical chemistry, the first of which will be held in October next. In this connection he expressed the hope that the Institute would in future have for its Presidents industrial chemists, as well as those eminent for educational and strictly professional work. The chief function of the Institute was to register competent consulting, analytical and technical chemists, and the Institute might safely claim to represent the profession. The Council regarded it as their duty to advance the interests of the profession, and, as far as they were able, to maintain it on a sound and satisfactory basis. They had lately been obliged to make representations to authorities whose actions appeared to be detrimental to the profession.

With reference to the gratuitous performance of analyses at agricultural colleges, he mentioned that the Board of Agriculture had endeavoured to show that the performance of cheap milk tests had been arranged for educational purposes. At the same time the Board had stated that these tests were not seriously to be compared with the analyses made by public analysts and district analysts. The Council had to complain of more than the milk tests : the colleges were undertaking all kinds of analyses at nominal fees--of soils, for instance, at half a crown. This was undoubtedly injurious to the profession ; but the Board, in its journal, stated that " the demand on the part of landowners for expert advice from the lecturers had been considerably in excess of what might reasonably have been anticipated." In this matter the Council had not received a satisfactory response.

He referred to the great advances in chemistry that had been due to the work of private practitioners, giving his opinion that any action which tends to interfere with the individual practitioners would be fatal to progress.

It was with reluctance that the Council had to take up an attitude which might seem in any way antagonistic to the National Physical Laboratory, but they had been obliged to direct the attention of the Executive Committee to the fact that their test pamphlet indicated that they might undertake work which they were forbidden to undertake under the Treasury Report on which the laboratory was founded. The Executive Committee has recently given their assurance of their desire to avoid any cause for complaint. He was sure that the Council would be glad to see the laboratory placed on such a sound footing financially that its authorities would have no temptation to extend the work of the laboratory beyond its proper sphere.

Mr. HOWARD thought the profession had reached a somewhat critical stage in its history. With greater facilities for training and, consequently, a larger supply of chemists, it was evident that only the most efficient could hope to be successful.

He believed the demand for chemists was increasing, but authorities and manufacturers were learning that they must have efficiency.

After dealing briefly with the present position of the industrial chemist and the official professional chemist, he referred to the professors and teachers of chemistry He objected to the practice, which had grown of late, of blaming the Universities for the loss of certain industries. He maintained that, while chemists were improving so greatly in efficiency, it was absurd to blame the professors. Every decade does not bring a Hofmann, but there were many teachers at the present day under whom the bulk of Fellows and Associates were proud to say they had been trained.

The Institute afforded a great benefit to the public by aiding its discrimination in the selection of competent chemists of acknowledged ability and professional integrity ; they could rely on each Fellow and Associate to further the reputation of the Institute by his character and conduct, the soundness of his work, and by the cultivation of professional feeling.

Mr. HOWARD then referred to the new President, Professor Percy F. Frankland, who had long been associated with the Institute, and whose father, Sir Edward Frankland, was the founder and first President. He concluded by saying how much he had appreciated his position as President of the Institute, and he spoke in warm terms of the co-operation of the Councils with whom he had worked

A vote of thanks for the address was moved by Mr. THOMAS TYRER, seconded by Professor J. MILLAR THOMSON, supported by Mr. R. J. FRISWELL, and carried unanimously.

On the report of the scrutineers the result of the balloting for the selection of censors was submitted, and Mr. David Howard ; Sir William Ramsay, K.C.B., F.R.S. ; Thomas Stevenson, M.D. ; and Professor J. Millar Thomson, F.R.S., were declared elected.

The officers and members of Council for the ensuing year were then declared elected, as follows :

President: Percy Faraday Frankland, LL.D., Ph.D., F.R.S. *Vice-Presidents:* Edward John Bevan ; Edward Divers, M.D., D.Sc., F.R.S. ; David Howard ; Edmund Albert Letts, D.Sc. ; Edmund James Mills, D.Sc., F.R.S. , Sir William Ramsay, K.C.B., LL.D., F.R.S. *Hon. Treasurer:* Alfred Gordon Salamon, A.R.S.M. *Members of Council:* Adrian John Brown, M.Sc. ; Lieut.-Colonel Charles Edward Cassal ; Arthur Crozier Claudet, A.R.S.M. ; John Norman Collie, Ph.D., F.R.S. ; James Kear Colwell ; Cecil Howard Cribb, B.Sc. ; Henry John Horstman Fenton, M.A., F.R.S. ; Martin Onslow Forster, D.Sc., F.R.S. ; Richard John Friswell ; William Gowland, A.R.S.M. ; Arthur George Green ; Henry George Greenish ; Oscar Guttmann ; James Hendrick, B.Sc. ; Egbert Grant Hooper ; Herbert Jackson ; Arthur Robert Ling ; Henry de Mosenthal ; Henry Droop Richmond ; Alfred Smetham ; Arthur Smithells, B.Sc., F.R.S. ; John Edward Stead, F.R.S. ; David Alexander Sutherland ; Francis Napier Sutton ; Edward William Voelcker, A.R.S.M. ; William Palmer Wynne, D.Sc., F.R.S. ; Sydney Young, D.Sc., F.R.S.

On the motion of Lieut.-Colonel CHARLES E. CASSAL, seconded by Mr. P. GERALD SANFORD, a vote of thanks was accorded to the retiring officers and members of Council. The PRESIDENT having replied, the meeting terminated.

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE PURIFICATION OF ZINC AND HYDROCHLORIC ACID FROM ARSENIC.

By L. T. Thorne, Ph.D., and E. H. Jeffers.

(Read at the Meeting, February 7, 1906.)

1. *Zinc.*—Hehner first suggested (Analyst, 1902, 261) the treatment of zinc with sodium for the purpose of removing traces of arsenic, but the method was somewhat uncertain. owing to the exact conditions necessary not being ascertained. Later we described before this Society conditions of this treatment under which we obtained reliable results; but as the manipulation we then used was complicated, we delayed printing the details, in order, if possible, to simplify it. After long trials and use we now lay before the Society the simplest conditions which we find reliable.

Commercially pure zinc is melted in a crucible in a gas furnace, and when at or only just above its melting-point sodium is mixed with it in the proportion of about 1 gram to each pound of zinc. This is best effected by adding the sodium in pieces of 1 to 2 grams weight which have not been dried from the adhering petroleum in which the sodium is stored. If the zinc be at the right temperature (*i.e.*, not too hot) the sodium is dissolved without•either it or the petroleum vapour becoming ignited. After all the sodium has been added, it is preferable to add a small piece of zinc to insure the temperature being reduced to about the melting-point. The crucible is heated for a few minutes till the zinc is completely fluid, and the zinc is then poured into a second previously heated crucible, and back again once or twice to insure thorough melting. If the temperature is not allowed to get too high practically no oxidation takes place during this transference. The crucible, with the lid on, is then put back into the furnace and heated to a dull red heat, when the furnace and crucible lids are both removed, and the heating is continued for at least half an hour (preferably for an hour), care being taken that the temperature should not rise much. A scum (or alloy) gradually rises to the top and forms a hard, dark gray crust on the surface about $\frac{1}{8}$ inch thick. This crust contains practically all the arsenic and the greater part of the sodium in combination with zinc. The crucible is allowed to cool slightly, the crust is pierced at one side, and the molten mass is poured into a second previously heated crucible and skimmed if necessary. This crucible is then heated to bright redness, any slight scum removed, then allowed to cool, and the zinc granulated just before the solidifying-point is reached.

The essential points for success appear to be to get as thorough mixing as possible at a low temperature, and to avoid material rise in temperature whilst the scum or alloy is forming and rising. The arsenic sodium and zinc compound seems to be most stable at somewhere near the melting-point of zinc, and to be partially broken up at high temperatures. The temperature, before the scum is removed, should not be hot enough for the zinc or scum to take fire when the crucible lid is removed.

In this way zinc absolutely free from arsenic is obtained, which gives in the Marsh-Berzelius apparatus a perfect blank with the solution of 15 to 20 grams of zinc, and is yet so sensitive as to give a definite and reliable result with 0·000002 grams of arsenious oxide, and the sensitiveness is always the same. The yield is about 95 per cent. of the zinc taken.

2. *Hydrochloric Acid.* —In 1902 we described (*Proc. Chem. Soc.*, 1902, 118) a method for the freeing of hydrochloric acid from arsenic by a modification of the Reinsch test. In use we found the presence of a little stannous chloride (*i.e.*, of a strong reducing agent) greatly facilitated the deposition of the arsenic on the copper gauze, lessened the amount of copper dissolved, and shortened the process, but it still remained somewhat tedious. Noticing the great effect of the tin, we then tried the employment of a copper-tin couple with complete success.

Redistilled hydrochloric acid is diluted to rather under a specific gravity of 1,100 (water = 1,000), and is then poured on to a copper-tin couple, prepared by reducing with zinc a mixture of copper and tin chlorides in hydrochloric acid and washing the precipitated spongy couple. The metals are used in about the proportion of 1 part by weight of tin to 4 to 8 parts by weight of copper. A convenient mode of preparing the couple is as follows: Cuprous chloride is dissolved in excess of hydrochloric acid, and a small quantity of granulated tin added. The tin rapidly dissolves, at the same time reducing some copper in a spongy form. Zinc dust, or the smaller portions of granulated zinc, is then added, and this reduces the remainder of the copper together with the tin in the form of a dark gray spongy couple, which is washed by decantation. Ordinarily pure cuprous chloride and tin may be used, as traces of arsenic which may be present are eliminated, and do not affect the final result. The couple may also be readily obtained by reducing with zinc the residual liquor in the distilling flask, which consists of the mixed chlorides. The couple should be gray in colour; if it is nearly black the copper is in too great excess. About 2 or 3 grammes of the couple are used to each litre of the diluted acid. The acid containing the couple is gradually heated, a strong reaction taking place at about 70° C., and kept on the boil for about a quarter to half an hour. During this time most of the tin and a part of the copper is dissolved, and practically the whole of the arsenic is evolved. The acid may then be distilled direct, or be cooled and kept under a layer of petroleum (to prevent absorption of oxygen); but in the latter case it must be distilled within twenty-four hours, or partial oxidation will occur. In the distilling-flask a small quantity of the couple should be placed, and also a small piece of 100-mesh copper gauze. This latter determines the precipitation of any minute traces of arsenic which may have escaped elimination by the preceding treatment, and also prevents bumping. The distilled acid is perfectly free from arsenic.

Good commercial muriatic acid may also be used, but in this case the first treat-ment must be repeated twice, as, owing to the traces of iron chloride and other impurities contained in the acid, the first lot of couple is generally completely dissolved, and does not fully eliminate the arsenic.

The residue in the distilling-flask serves conveniently for the preparation of fresh copper-tin couple, as the proportion in which these two metals are present in the couple is not important.

DISCUSSION.

The PRESIDENT (Mr. Bevan) having invited discussion,

Mr. HEHNER desired personally to thank the authors for laying down the conditions under which the sodium treatment was fully successful. As he had explained a few years ago, he had often succeeded in purifying satisfactorily very bad zinc by treatment with sodium, but he had often failed to improve materially even comparatively pure zinc. He had not, however, had so much patience as the authors, and so had never ascertained the exact conditions that were necessary. He was very glad now to find that the authors had brought what was formerly an entirely rule-of-thumb process into something like law and order.

Mr. CHAPMAN said that his own experience was that it was now rarely necessary to purify zinc from arsenic, the great difficulty at the present time being to get zinc that would give out the full amount of arsenic that was put in. Consequently, the problem was not quite so urgent a one as it was when Mr. Hehner took the matter up a few years ago. There could, he thought, be no doubt whatever that the sodium method, if properly applied, was capable of removing the arsenic. He himself had sometimes been unsuccessful with it, but that was probably because he had not known the precise conditions necessary for success. The many experiments he had made, however, went to show that, unless the sodium was entirely removed, the zinc obtained was distinctly "insensitive." He thought that that was proved by the mirrors which the authors had shown. For example, their mirror for the $\frac{1}{100}$ mgm. of arsenic was not more than half that which he was in the habit of getting, and which he had every reason to believe to be correct. The same applied to the other mirrors. Through the kindness of Dr. Thorne, he had had the opportunity of examining some of this sodium-treated zinc with his own materials, and the conclusion he came to was that it was distinctly insensitive. If, therefore, the sodium treatment was to be employed, it must be with very great care, and the operator must recognise the possibility, or even probability, of the resulting zinc being more or less insensitive. The method for the purification of hydrochloric acid recommended by the joint committee of the Society of Chemical Industry and the Society of Public Analysts (treatment with bromine and sulphurous acid and distillation) in some cases worked well, but in others did not. He had, however, for some time been invariably successful in purifying the most impure acid by a slight modification of that method. The only modification was that the strong acid was distilled, instead of being first diluted down to constant boiling-point strength. The pure acid obtained amounted to about three-fifths of the total quantity treated. The only failure he had had was due to the mechanical carrying over of a little iron into the distillate from a very

impure acid. This, as had been recently shown, caused diminished sensitiveness, but it was easily obviated by a suitable arrangement of the distilling apparatus.

Dr. DYER said that Mr. Chapman had anticipated a remark that he had been about to make regarding the faintness of the authors' mirrors. Their mirror from $\frac{1}{100}$ mgm. appeared to be less than the mirror obtained in his laboratory from half that quantity of arsenic, working with acid which gave a good blank, and using tubes of approximately the same size as those shown. That seemed to point to slight insensitiveness of the authors' zinc.

Mr. H. D. LAW said that, from the results of the investigation recently communicated to the Society by Mr. Chapman and himself, it was evident that sodium was one of those metals which seriously interfered with the sensitiveness of zinc. He had since made some experiments to find out the particular reducing efficiency of hydrogen liberated by sodium and potassium. By passing an electric current through a solution of sodium hydroxide or potassium hydroxide, a deposit of sodium or potassium was obtained. This dissolved in the water, with liberation of hydrogen at the potential of the metal. The reducing power of this hydrogen had been compared with that of the hydrogen liberated by various metals of different potentials. Camphor was very readily reduced with lead electrodes, but when he tried to reduce camphor with the hydrogen liberated by sodium or potassium, he found that he was quite unable to do so. This showed that the potential of the sodium or potassium was very much lower than that of zinc or lead. He then took different materials which were capable of being readily reduced, such as benzaldehyde, in order to find out, by lowering the reducing potential, at what point a degree of reduction was obtained corresponding with that produced by sodium hydrogen. With lead electrodes benzaldehyde yielded a very sticky mass quite characteristic of high-potential reduction, while with metals of lower potential the sticky masses produced were very much less in quantity. Finally, he took refined copper electrodes, which yielded no sticky substance at all, but a crystalline, brittle hydrobenzoin corresponding to that obtained by reduction in sodium and potassium solutions. This proved conclusively, he thought, that the potential of sodium and potassium was about the same as that of copper, which was extremely low.

Dr. THORNE said that he was inclined to think that, if there was any diminution at all in the sensitiveness of the zinc, it was but very slight. Personally, he was strongly of opinion that in many cases where zinc was said to be highly sensitive either it or the acid was not absolutely free from arsenic. He had certainly not had the same success as Mr. Chapman in obtaining zinc that would give an absolutely clear blank without repurification, though there had undoubtedly been a great improvement in commercial zinc during recent years. As a test of the absolute purity of the zinc, they ran blank determinations for an hour and a half. A twenty-minutes' blank might to a certain extent be satisfactory, but they had found after a large experience that the very small traces of arsenic which were present in most commercial zincs tended to cause irregular results, giving undue prominence to small quantities as compared with larger quantities of arsenic in the material under examination. They found the sensitiveness of each successive batch of zinc purified to be practically the same, and although he was quite prepared to admit that the

mirrors they obtained might be slightly less intense than the small-quantity mirrors obtained with other zincs, he thought that the continuous concordance of the mirrors after repeated treatments with sodium showed that they were truly representative, and that the danger of loss of sensitiveness by the treatment was practically nil. The more strongly marked character of the low-quantity mirrors in other cases was probably due, in part at any rate, to traces of arsenic in the other materials. With reference to Mr. Hehner's remarks, he should like to say that a good deal of the patience expended on this matter had been that of his collaborator, Mr. Jeffers. With regard to hydrochloric acid, they also had found that the method first proposed by the joint committee did not answer in all cases. They did not say that the method they had described was a better one than the committee's method as now modified, but it had been found reliable with ordinary impure acid as well as with acid of good quality, and was a simple and convenient method.

In answer to a question put by Dr. Dyer, Dr. Thorne said that they had not tried Mr. Chapman's device of introducing cadmium sulphate into the flask.

Mr. Chapman said that he could put forward in support of his own contention exactly the same argument which Dr. Thorne had used. The mirrors he obtained were perfectly concordant, whatever the method or materials were. Sometimes he put cane-sugar, soluble starch, etc., into the flask, sometimes he left it out; but the mirrors in either case were always of the same intensity within the very narrow limits of experimental error. He asked what evidence there was that the appearance of a bright surface on the zinc coincided with the disappearance of the whole of the sodium.

Mr. Jeffers said that he did not think it could exist alongside the zinc at that temperature.

Mr. Chapman said that it might quite well exist in very small quantity as an alloy dissolved in the zinc.

Mr. Jeffers said there was no room for doubt as to the complete removal of the sodium. If the sodium were not entirely removed, it was impossible to get a bright surface on the zinc at a red heat.

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NOTE ON DUTCH CHEESE.

By CECIL H. CRIBB, B.Sc., F.I.C.

(Read at the Meeting, February 7, 1906.)

In the earlier part of last year I received, amongst a number of other samples of Dutch cheese submitted to me under the Sale of Food and Drugs Acts, some which contained extremely minute proportions of fat. In view of the general recognition of the fact that Dutch cheese is not made, except in the case of certain well-defined brands, from whole milk, it became necessary to consider whether the sale of such samples brought the vendors within the provisions of the Act—*i.e.*, whether they should be regarded as genuine or adulterated.

On looking up the literature of the subject, the question seemed fairly simple. Practically all the published analyses give proportions of fat far exceeding those in the samples I have just referred to, the figures given in every case but one ranging from 19 to 33 per cent. The sole exception to this occurred in a paper by Messrs. Pearmain and Moor (ANALYST, xix., 145), where a fat content of 10·6 per cent. is recorded. I also found that during the last four or five years there have been several prosecutions for selling, either as Dutch cheese or as cheese, samples which were more or less deficient in fat (*British Food Journal*, 1900, p. 47; 1901, p. 202; 1903, pp. 90, 159, 164, 229); and in those cases in which Dutch cheese had been specifically asked for, and in which the proportion of fat was at all comparable with that in the cheeses examined by myself, a penalty was inflicted. I felt justified under these circumstances in certifying adulteration, and proceedings were instituted against the vendors. Counsel appeared for both sides, and after a somewhat protracted trial the magistrate decided that there was no standard, and that the prosecutor had therefore been supplied with cheese which was of the nature, substance, and quality demanded. As during the hearing of some of the cases referred to above, somewhat widely varying opinions had been expressed as to the amount of fat *Dutch* cheese should contain, I thought it desirable to get some idea as to the range of fat content in the Dutch cheese which was actually being imported into the country at the time, and by the kindness of two of the largest firms in the wholesale trade I obtained a series of samples which fairly represent every price and quality coming over at that particular date, the results of analysis of which, together with those of the official samples submitted to me, are given in the following table:

I. From Wholesale Houses.

	Wholesale Price per Cwt.	Approximate Retail Price per Pound.	Fat.	N 6·38.	Ash.	Water.
1. Gouda ...	28s.	4d. to 5d.	1·64	—	5·71	55·22
2. Edam ...	30s.	,,	3·83	25·34	5·81	60·38
3. ,, ...	34s.	,,	4·04	31·92	7·33	53·66
4. Gouda ...	28s.	,,	5·01	28·53	5·29	54·26
5. ,, ...	28s.	,,	5·02	24·89	7·30	58·26
6. ,, ...	32s.	5d. to 6d.	5·36	22·05	5·30	59·28
7. ,, ...	34s.	,,	4·56	31·22	6·10	54·83
8. ,, ...	34s.	,,	4·73	25·34	6·26	60·17
9. Derby shape...	36s.	6d.	4·75	31·92	5·67	54·10
10. Gouda ...	38s.	,,	13·6	23·91	5·48	56·15
11. ,, ...	42s.	,,	12·45	26·67	5·43	50·46
12. ,, ...	44s.	,,	13·2	25·34	4·26	50·63
13. ,, ...	42s.	,,	15·3	23·90	5·15	50·96
14. ,, ...	42s.	,,	18·37	24·54	4·48	52·45
15. Derby ...	46s.	7d. to 8d.	15·95	24·37	5·27	49·45
16. Edam ...	52s.	,,	15·12	24·00	5·54	52·50
17. Edam (full cream) ...	58s.	8d.	24·4	26·05	5·58	41·70
18. "Case" cheese	65s. 4d.	10d. to 1s.	27·9	21·89	4·28	46·2

II. Official Samples.

	Fat.	N 6·33.	Ash.	Water.
19.	1·89	36·24	7·47	56·89
20.	2·75	31·02	8·82	55·40
21.	5·20	31·37	7·15	53·80
22.	2 65	38·46	10·8	51·90
23.	6·62	26·85	6·47	58·80
24.	15·40	---	6·07	50·14
25.	27·12	· ·	5·94	43·70

The most striking thing about these figures is the vast difference between the proportions of fat occurring in my samples and that found by the various authors to whom I have previously referred. For, excepting Messrs. Pearmain and Moor, all previous observers seem to have found what, judging from my analyses, must be regarded as the maximum figures for fat. It seems clear that a great change had taken place in the composition of Dutch cheese since the earlier analyses were made.

I was informed that the great bulk of the trade is concerned with cheese of the quality represented by the samples numbered 10 to 16, and that at the time the samples were given to me the total bulk of this quality which was sold amounted to fifty times as much as that of the poorer kinds represented by numbers 1 to 9. I was also told that the greater part of the latter was imported into England for one large retail firm, with branches all over the country, who, by selling this inferior article, were gradually forcing their poorer competitors to deal in goods which they would formerly have refused to touch, and thus the whole trade was gradually becoming demoralized.

It is quite obvious from the proportions of fat they contain that the samples numbered 1 to 9 really represent a class of product altogether different from numbers 10 to 16, and are plainly made entirely from separated milk. Considering that the cheeses were valued almost entirely by the unaided senses, it is remarkable how closely the proportions of fat run parallel with the price; and although in many cases a larger percentage of fat was expected than actually turned out to be present, there is no reason to suppose that an expert buyer would be under the slightest delusion as to what he was getting if he came across any of the first nine samples on the list. On the other hand, the ordinary householder would probably fail to see any difference between members of the first and second groups.

As the main point in the defence was the absence of an official standard for cheese, the local authority for whom I acted addressed the Board of Agriculture on the subject, and requested that they would consider the advisability of fixing such a standard. Similar action was at the same time taken by a large number of county and borough councils throughout the country. namely, at the instigation of the Council for the County Borough of Bournemouth.

In response to these communications a letter was received from the Board of Agriculture, saying that "there were difficulties in the way of framing suitable

regulations of the nature desired," owing to the existence of so many different varieties of cheese, and that it was not clear in what way such regulations "would assist consumers in obtaining the article they desire." They state that, "on consideration of all the circumstances," they did not feel that "any advantage would be gained by the attempt to deal with cheese by the issue of regulations under the Act."

This decidedly unsatisfactory document entirely fails to answer the question to which I want to direct attention in the present communication—namely, Should the sale of these separated-milk Dutch cheeses be held to constitute adulteration? The question is not merely the academic one of clerical procedure, but involves a matter of much greater importance. If the Board of Agriculture, having power to fix standards, do not use it, their failure to do so is likely to prove a most serious hindrance to the proper administration of the Acts. Before the 1899 Act came into force the magistrate relied almost entirely on the Public Analysts for information as to what constituted adulteration, but now the first question he asks is usually, What is the Government standard? And if there is not one, he in many cases at once concludes that the Government have refrained from fixing one because they were unable, and not because they had never tried, the obvious conclusion being that, if they had failed, no one else could succeed.

It is quite plain that now the reply of the Board of Agriculture has become more or less public property, the analyst who attempts to support a prosecution in the case of a separated-milk Dutch cheese will be in a much more difficult position than he would have been in before that reply was issued. Whatever the law may have to say on the subject, the Public Analyst is bound to report the sample as either genuine or adulterated, as the Act recognises no halfway house between the two. Put quite briefly, I personally think that such samples as those referred to should be returned as adulterated for the following reasons: Dutch cheese has been known for a very large number of years, and its reputation was built up during a period when such products as some of the worst samples were practically unknown, or, if they existed, were openly sold as *skimmed* or *separated* milk cheese. It is used, not as a condiment, but as a cheap and convenient source of nourishment, mainly by the poorer classes, and in probably the greater number of cases without butter being taken at the same time, so that the almost complete absence of fat interferes seriously with its digestibility. Apart altogether from this, the great deficiency of fat carries with it other defects, which are most distinctly to the prejudice of the purchaser. The most important of these is the fact that the presence of so little fat enables the cheese to retain a much larger amount of water without betraying the fact in any way, and as a further result it dries much more rapidly, and in a short time gets so hard that it can only be cut with a hammer and chisel.

The obvious explanation of the poor quality of much of the Dutch cheese now on the market is to be found in the use of separated instead of skimmed milk. As far as my information goes, all the reputable kinds of Dutch cheese were formerly made either from whole milk or from the whole morning milk mixed with the skimmed milk of the previous evening. Now that cheese is mainly the product of a factory instead of a farm, it is not likely that the old and inefficient process of hand-

skimming is employed at all, so that even if the old traditions were adhered to as regards the cheeses other than those made from whole milk, there would be a lowering of the fat content to at least the extent shown by my analyses.

As these facts are not known to the public, it seems to me that this is a case, if ever there was one, in which the Board of Agriculture should exercise its powers, especially as the objections it advances to fixing standards are by no means convincing, and, so far as Dutch cheese is concerned, have but little force.

DISCUSSION.

The PRESIDENT (Mr. Bevan), in inviting discussion, said that, personally, he thought that the justice of the case would be met if cheese made from skimmed milk were required to be so labelled.

Dr. VAN RIJN said that, as Mr. Cribb had already very clearly explained, a good deal of cheese had been sent over from Holland lately during the last year or so— which contained only a very small proportion of fat. The reason for this was that in some parts of Holland, where several years ago no cheese at all used to be made, all the separated milk was now used for making cheese. A market was found for it over there at the price it was worth, but, of course, the people who made it could not be responsible for what was done with it later on. He personally thought that it was not fair to sell this "separated cheese," as he would call it, simply under the name of Dutch cheese. It was, however, very difficult he thought almost impossible- to fix a legal standard for cheese generally. Something in that direction had been attempted in Holland, and now combinations of cheesemakers were being formed for the purpose of doing what had been done with regard to butter control— namely, to fix a standard for themselves and to establish stamps or marks for their cheeses. For instance, it would not be permissible to make a cheese of the ordinary Gouda or Edam shape containing less than about 15 per cent. of fat (25 per cent. fat in the dry residue). He thought that the majority of the cheesemakers at the moment were in favour of such a limit. It would not have any legal force, but would be a commercial standard. If it were adopted it would naturally strengthen greatly the position of the authorities in such prosecutions as had been lately instituted in this country. He should like to explain why so low a limit as about 15 per cent. was suggested. For Edam cheese it was the custom to mix the evening milk, after the cream had been taken off, with the full-cream morning milk, and to make the cheese from this mixture, which contained, especially at some seasons of the year, a somewhat low proportion of fat. From experiments made with normal milk of varying degrees of richness at a Government station in Holland, the lowest proportion of fat in cheese made in this way was found to be 20 per cent. The lower limit of 15 per cent. was proposed in order that a margin might be allowed to cover possible abnormalities in the milk used. It was, moreover, possible to make good cheese containing this amount of fat. With a much smaller quantity of fat the quality of the cheese was quite different. He did not know much about the digestibility of cheese containing only a few per cent. of fat, but it certainly was not a first-class commercial product.

The question of the estimation of fat in cheese had been already mentioned in the ANALYST about a year ago. He had just had an opportunity of discussing it with one or two colleagues, whose opinion had been that the same results would be obtained whichever of the ordinary methods might be used. This was, practically speaking, correct in the case of full-cream cheese containing from 30 to 40 per cent. of fat, but it had been stated very clearly in Holland by several analysts that, with cheese containing a low percentage of fat (below 22 per cent.), the method of extraction with ether always yielded 2 or 3 per cent. less fat than was actually present. He might perhaps later on have something to add in reference to this.

Mr. HEHNER said that many years ago he had called attention to this problem, because it seemed to him very anomalous that, while a man was allowed to sell cheese made from milk from which the fat had been taken, as soon as he tried to confer a benefit on the purchaser by filling up the cheese with other fat he was punished. He thought it unreasonable to punish the vendor of margarine cheese while leaving the vendor of skimmed-milk cheese free. He had never found any difficulty in distinguishing by taste and appearance between skimmed-milk cheese and full-cream cheese, but a "filled" cheese was very difficult to distinguish without chemical analysis. At one time cheese might fairly be considered to be, roughly, one-third water, one-third fat, and one-third other things. But times had since changed considerably. Cheese was now one of those manufactured products which allowed the maker a good deal of scope; and the courts had laid down—he thought rightly—that the manufacturer had a right to exercise his ingenuity in the manufacture and composition of a manufactured product. A food material that was virtually sold as Nature furnished it must be as Nature gave it, but as soon as the question of manufacture came in there must necessarily be a certain latitude. That was the case with cheese and with many other things. It was, however, very difficult in a case like that of cheese to give a notice consistently. It was imaginable that boxes should be branded, but it was almost impossible to mark each piece of cheese sold. If, however, some means could be introduced for distinguishing at once—say, by colour —between full-cream cheese and skimmed-milk cheese it would probably be a boon to the consumer. But the Dutch manufacturers were very scientific, and understood very well how to sell both butter and cheese at the same time at a good price, and it would be much better that they should, in the way that Dr. van Rijn had mentioned, themselves take steps to guard against the mischief resulting from too acute competition. He thought that everybody must agree with Sir Thomas Elliott that it was exceedingly difficult to lay down a general law. Several kinds of cheese had, by common consent, been allowed to be made from skimmed milk—for example, Parmesan, Dutch, and some Dorset cheeses—and, after all, what one person had the right to do could not well be denied to another. In fact, he had gradually come to consider that cheese was now one of those products which were entirely manufactured, and that the question was one in which the public and not the analyst must be the final arbiter.

Mr. JOHN WHITE thought that all that Mr. Cribb wanted was what he himself had wanted when he was concerned in a similar campaign which had resulted disastrously—namely, not to stop the sale of the article, but to let it be sold for what

it was, viz., skim-milk cheese. It was right that the skill of the manufacturer should be taken into account, provided that the article made was being improved ; but here the skill of the manufacturer had been employed to produce, not an improved article, but one of diminished value. With regard to the position of the public as the ultimate arbiter, he could not conceive that anybody would buy this stuff a second time. After being kept for two or three days it became exceedingly hard. Personally, he considered it a gross fraud to sell as cheese, or as Dutch cheese, an article containing only 1·6 per cent. of fat. As to the estimation of the fat, he had found that such small quantities could only be accurately determined by what was practically the Werner-Schmidt process—namely, by boiling with water and hydrochloric acid, cooling, and shaking out with ether.

Mr. Fisher drew attention to the results shown by a sample purchased as Dutch cheese, which he had analysed in 1903. It contained only 1·6 per cent. of fat, with 57·1 per cent. of water and the vendor was in consequence fined £10.

Mr. Cribb, in reply, said that he had adopted practically the same method of fat estimation as Mr. White. He could confirm what Dr. van Rijn had said as to direct extraction with ether. When the quantity of fat was large the error was, for practical purposes, of no consequence, but with a small percentage of fat the error, which was still about the same in absolute weight, bore a larger proportion to the total. It seemed to him that if the manufacturer of cheese were to have an entirely free hand he might make an article containing nothing but casein, water, and a little mineral matter, but nobody would pretend that to the consumer that was Dutch cheese as ordinarily understood. As to the suggested difficulty of notification, he could not see any difference between the case of cheese and that of butter and margarine, with regard to which provisions as to labelling were already in existence. If the Sale of Food and Drugs Acts were carried out properly, any radical change in a well-known article of food would be discovered at once. Under the present conditions any such change was, as a rule, not found out until it had been so long in operation as to become an established trade custom, which could not be altered without inconvenience and loss to many. All this pointed to the necessity for a more thorough application of the Sale of Food and Drugs Acts, and for the taking of much larger numbers of samples than were taken November 22, 1906.

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ORDINARY MEETING OF THE SOCIETY.

This was held on Wednesday evening, March 7, in the Chemical Society's Rooms, Burlington House. The President, Mr. E. J. Bevan, occupied the chair.

The minutes of the previous meeting were read and confirmed.

Certificates of proposal for election to membership in favour of Messrs. G. Craig, J. B. Gall, H. N. Hanson, B. W. Methley, F. D. Ratcliff, and F. Robertson, were read for the second time ; and certificates in favour of Messrs. Ernest Quant, 2, Park

Crescent, Torquay, analytical chemist; Frederick Wilson Montrose Ross, 21, Soho Square, London, W., analyst to Messrs. Crosse and Blackwell, Ltd.; and Frank Ernest Thompson, A.R.C.Sc., A.I.C., the Laboratory, Walsall, analytical and consulting chemist, were read for the first time.

Messrs. S. Dickson, J. Evans, F. Hughes, G. Patterson, and H. Thompson, were elected members of the Society.

The following papers were read: " A Simple and Rapid Method for the approximate Estimation of Boric Acid," by Cecil H. Cribb, B.Sc., and F. W. F. Arnaud; " Analysis of a Sample of Air extinguishing Flame," by Bertram Blount; " The Detection of Cocoanut Oil in Butter," by Arthur W. Thorp; and " The Composition of Milk," by H. Droop Richmond.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

A New Centrifugal Method for Determining Fat in Milk — Wendler's Method. Von Küttner and Ulrich. (*Zeit. offentl. Chem.*, 1906, xii., 41-58.)—The process consists in mixing the milk with a saline solution, adding a little isobutyl alcohol, and subjecting the mixture to centrifugal action, the procedure being similar to that of Gerber's method. The saline solution employed contains tartrates, sodium chloride, and sodium hydroxide (proportions not given). Eleven c.c. of this solution, 10 c.c. of the milk to be tested, and 0·6 c.c. of isobutyl alcohol are successively introduced into a butyrometer tube and the latter then closed with an indiarubber stopper. The contents of the tube are mixed, the tube is immersed for two or three minutes in water at a temperature of 45° C., and then submitted to centrifugal action in the usual way. The surface separating the fat from the saline solution is quite horizontal, rendering the reading of the volume of the fat an easy matter. If the contents of the tube have been well mixed, no flocculent layer ever occurs between the fatty and aqueous layers. The results obtained, as shown by 360 comparative determinations, agree with those yielded by Gerber's method.   W. P. S.

A Rapid Method for the Detection of Traces of Zinc in Wort, Beer, Wine, etc. J. Brand. (*Ztschr. ges Brauw.*, 1905, xxviii., 410; through *Chem. Zeit. Rep.*, 1906, xxx., 25.)—The liquid to be examined is acidulated with hydrochloric acid, and a few drops of potassium ferrocyanide solution are added. The presence of even a trace of zinc will cause a flocculent precipitate of zinc ferrocyanide to be produced, which, being mixed with much albumin, settles rapidly, and may be readily filtered after decanting the bulk of the liquid. The washed precipitate is ignited, and the

residue treated with acetic acid; in the solution obtained zinc is identified with hydrogen sulphide. As little as 1 part of zinc in 500,000 parts of beer, etc., can be readily detected by this method. A. G. L.

Hordenine: A New Alkaloid extracted from the Germ of Barley.

E. Léger. (*Journ. Pharm. Chim.*, 1906, xxiii., 177-181.)—A crystalline alkaloid has been separated by the author from the dried germs of malted barley. It was first obtained in ethereal solution by means of Stas' method, and the residue left on evaporation purified by repeated crystallization from alcohol and decolorized with animal charcoal. The yield of *hordenine* appears to vary with the temperature at which the malt was dried, and the author has obtained from 0·22 to 0·45 or 0·5 per cent. from different germs. The alkaloid crystallizes in orthorhombic prisms, which show double refraction. They are anhydrous, colourless, and almost tasteless, and melt at 117·8° C. (corr.) to a colourless liquid. Hordenine slowly sublimes at its melting-point and rapidly at 140° to 150°. It is readily soluble in alcohol, chloroform, and ether, less soluble in benzene, only slightly soluble in water, and almost insoluble in cold petroleum hydrocarbons. It dissolves easily in hot carbon tetrachloride, but separates out almost quantitatively on cooling. It acts as a strong base, giving a red coloration with phenolphthalein and displacing ammonium from its salts in the cold. It gives no coloration with strong sulphuric acid, and is hardly attacked by a hot concentrated solution of potassium hydroxide. On the other hand, it reduces potassium permanganate in acid solution, hot silver nitrate solution, and iodic acid solution, yielding a precipitate of iodine. Its formula, calculated from the composition of its salts, is $C_{10}H_{15}NO$. It is a tertiary monoacid base, and thus forms only a single series of salts, all of which are very soluble in water. C. A. M.

Determination of Chloral Hydrate.

T. E. Wallis. (*Pharm. Journ.*, 1906, vol. 76, 162, 163.)—The method proposed consists in heating the chloral hydrate with sodium hydroxide in alcoholic solution and titrating the sodium chloride formed. The determination of the amount of sodium hydroxide absorbed gives untrustworthy results (*cf.* ANALYST, 1903, xxviii., 189), unless strict conditions be adhered to. The details of the method are as follows: A weighed portion of from 0·1 to 0·4 gram of the chloral hydrate is dissolved in about 10 c.c. of the alcohol, and introduced into a thick-walled bottle. A measured volume of $\frac{N}{1}$ sodium hydroxide solution is added, the bottle is closed by an indiarubber stopper, which is tied down, and the bottle with its contents heated for three hours in a water-bath. After cooling, the solution is neutralized with sulphuric acid, using phenolphthalein as indicator, and then titrated with $\frac{N}{10}$ silver nitrate solution. The reaction is represented by the equation,

$$CCl_3CH(OH)_2 + 5NaOH = 3NaCl + 2HCOONa + 3H_2O.$$
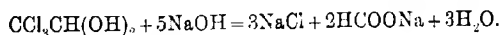
It is important that the contents of the bottle during the heating contain at least 50 per cent. of alcohol by volume. W. P. S.

The Determination of Traces of Chloroform. M. Nicloux. *(Comptes Rendus, 1906, cxlii., 163-165.)*—Chloroform when present in alcoholic solution in a quantity not exceeding 0·1 gram can be determined by diluting the liquid to 60 c.c. with alcohol, and boiling it for an hour under a reflux condenser with 10 c.c. of a 10 per cent. alcoholic solution of pure potassium hydroxide. When cold, the contents of the flask are mixed with 15 c.c. of water, exactly neutralized with phenolphthalein as indicator, and treated with potassium chromate, and the chlorine titrated with standard silver nitrate solution (8·535 grams per litre), each c.c. required representing 2 mgms. of chloroform. Air containing chloroform is analysed by being drawn through alcohol (95 per cent. strength), contained in two absorption vessels, at the rate of 1 litre in half an hour, and the absorbed chloroform is then determined as above described. In the case of blood and aqueous liquids it is necessary to add strong alcohol (80 to 95 per cent.), acidified with 0·25 gram of tartaric acid in the proportion of 5 parts to 1 of the sample, and to distil the mixture in a fractionating flask until about a third has passed over. The distillate is received in 10 c.c. of 95 per cent. alcohol, and the chloroform determined as before. The results thus obtained are invariably 1·5 to 2 per cent. too low. C. A. M.

The Constituents of Myrrh. A. Tschirch and W. Bergmann. *(Archiv. Pharm., ccxliii., 641 ; through Pharm. Journ., 1906, vol. 76, 128.)*—Picked Somali myrrh was found to have the following composition : Soluble in alcohol (resin and oil), 28 to 30 per cent. ; insoluble in alcohol (gum and enzyme), 61 per cent. ; impurities, 3 to 4 per cent. ; moisture, 5 per cent.

Part of the substances soluble in alcohol was insoluble in ether, the remainder (about 21 per cent. of the myrrh) being soluble. The portion insoluble in ether was redissolved in alcohol, and separated by precipitation with lead acetate into α-heerabo-myrrholol and β-heerabo-myrrholol, the latter remaining in solution. These substances were obtained in the form of yellowish-brown and grayish-brown amorphous powders respectively.

The portion of the alcoholic extract soluble in ether was dissolved in this solvent, and treated with potassium hydroxide to remove α-and β-heerabo-myrrhol, which were afterwards separated by means of lead acetate, when they were obtained as grayish-yellow powders. The ethereal solution was next evaporated and distilled in a current of steam. By this means a residue of heerabo-resene was obtained in the retort, whilst the distillate consisted of yellow oil. The latter had a specific gravity of 1·046, rapidly resinified, and bore no relation to the resin acids, resinotannols, resinols, etc., found in other resins.

The substances insoluble in alcohol, consisting of the gum and enzyme, could not be separated from one another. The gum yielded arabinose on hydrolysis. In addition to these substances, myrrh also contains a bitter principle, but all attempts to isolate it failed. W. P. S.

Determination of Cinnamic Acid in Storax. D. Hooper. *(Pharm. Journ., 1906, vol. 76, 107.)*—The determination of the amount of cinnamic acid in storax is proposed as a method of detecting the presence of adulterants in this balsam.

Tschirch and Itallie have shown that true Oriental storax contains 23 per cent. of cinnamic acid, and other investigators have concluded that the percentage of the acid should not fall below 20. A weighed quantity of the storax is saponified in alcoholic solution with potassium hydroxide, evaporated to remove the alcohol, the residue dissolved in water, and the solution shaken out with ether to remove unsaponifiable substances. The solution is then treated with sulphuric acid in excess, and the voluminous precipitate collected on a filter and washed. The precipitate is next dissolved in hot water, and the crystals which separate on cooling are collected, dried, and weighed.　　　　　　　　　　　　　　　　　　　　　W. P. S.

Adulterated Santal-Wood Oil. E. J. Parry. (*Chemist and Druggist*, 1906, lxviii., 211.)—The low price of large parcels of this oil imported from Germany caused suspicions to arise as to the purity of the oil, and the author has recently examined a sample which enabled him to definitely decide the nature of at least one of the adulterants present. The oil had a specific gravity of 0·970 at 15° C., an optical rotation of − 14° in a 100 mm. tube, was soluble in 5 volumes of 70 per cent. alcohol, and had an apparent santalol value (free) of 93·5. By repeated fractionation under reduced pressure a small amount (about 5 per cent.) was obtained, which boiled at 220° C. at ordinary pressure. The specific gravity of this fraction was 0·913, and the refractive index 1·4823 at 20° C. The odour left no doubt as to its being terpineol. This was confirmed by the melting-point (115° C.) of the nitroso-chloride yielded by the fraction.　　　　　　　　　　　　　　　　　W. P. S.

The Purity of Balsam of Peru. Utz. (*Pharm. Post.*, xxxix., 21 ; through *Pharm. Journ.*, vol. 76, 129.) -Adulteration of this balsam is, according to the author, the rule rather than the exception. Turpentine and gurjun balsam appear to be the favourite adulterants, and the usual tests often fail to detect them. Such adulterated balsams may show a cinnamein content of 50 to 60 per cent. The physical characters of the cinnamein obtained sometimes indicate sophistication. It should be brown and homogeneous, whereas with turpentine it is often granular or even solid. The refractive index gives more satisfactory results, as for pure balsam the value varies from 1·5862 to 1·5878 at 15° C. ; whilst the refractive index of gurjun balsam is 1·5142 ; of castor oil, 1·4809 ; and of paraffin oil, 1·4821. On the other hand, perugen, which is a factitious substitute for balsam of Peru, possesses a refractive index of 1·5863. Perugen, however, gives an intense olive-green coloration with Cæsar and Loretz's nitric acid test, instead of the golden yellow yielded by pure balsam of Peru.　　　　　　　　　　　　　　　　　　　　　W. P. S.

TOXICOLOGICAL ANALYSIS.

Toxicity of Cyanogen Compounds towards Fish. J. Hasenbaümer. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, vol. 11, 97-101.)—The author has carried out a considerable number of experiments regarding the action on fish of certain cyanogen compounds when the latter were added to the water in which the fish lived. The investigation was in connection with an inquiry regarding the discharge of effluent containing traces of these compounds. Potassium cyanide was found to be extremely

poisonous to fish, 0·0018 gram per litre of water killing tench and goldfish in a very short time The following quantities per litre of other cyanogen compounds also killed fish of these species : Potassium ferrocyanide, from 1·5 to 3·0 grams ; potassium ferricyanide, from about 1·7 gram ; potassium or ammonium thiocyanate, about 1·5 gram.   W. P. S.

ORGANIC ANALYSIS.

Temperature of Combustion of Methane in presence of Palladiumized Asbestos. H. J. Denham. *(Journ. Soc. Chem. Ind.,* 1905, xxiv., 1202.) — An investigation undertaken to ascertain to what extent methane is burnt when passed over palladiumized asbestos in presence of oxygen has shown that (1) the temperature of combustion of a mixture of 1 volume of methane with 2 volumes of oxygen lies between 514° and 516° ; (2) an increase in the speed at which the gases are passed through the tube causes a decided increase in the temperature of combustion ; (3) a variation in the volumes of the gases influences the temperature of combustion, tending to raise it beyond the above-mentioned range ; and (4) the addition of hydrogen, even in large quantities, does not cause the methane to burn at a lower temperature. It is concluded, therefore, that the usual method of fractional combustion of hydrogen gives reliable results, if the temperature does not exceed 500 to 550°. The catalytic action of the metal does not appear to be due to superficial oxidation, and in no case has anything approaching complete combustion been observed, even when the gas was 100° above its combustion temperature.

W. H. S.

The Volumetric Determination of Pentoses. A. Jolles. *(Berichte,* 1906, xxxix., 96, 97.)—From 0·2 to 1·0 gram of the substance under examination is treated with 200 c.c. of hydrochloric acid (specific gravity 1·06), and distilled in a current of steam until Bial's reagent shows that no more furfural is formed, an additional 100 c.c. of the hydrochloric acid being introduced into the flask during the distillation. The furfural is now determined in an aliquot part of the distillate by treating it, after neutralization, with a known excess of standard potassium bisulphite solution, and titrating the excess with standard iodine solution after the mixture has stood for two hours :

$$C_4H_3O.COH + HKSO_3 = C_4H_3O.CH(OH)SO_3K.$$
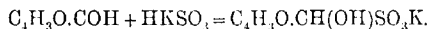
Each c.c. of normal bisulphite solution is equivalent to 0·07505 gram of pentose.

C. A. M.

The Detection of Olive Oil extracted by Means of Carbon Bisulphide in Soap. J. Vamvakas. *(Ann. de Chim. Anal.,* 1906, vol. 11, 53, 54.)—The soap manufactured in Crete is prepared almost exclusively from olive oil, and the author has long used the following simple method for determining whether the original oil had been extracted by means of carbon bisulphide : 2 grams of the soap are dissolved in 100 c.c. of 95 per cent. alcohol, the solution filtered, and its colour noted.   If colourless or gray the oil was obtained by mechanical expression, whilst a yellow colour (with green fluorescence) indicates soap prepared from an

extracted oil. The addition of a green or yellow dye stuff, soluble in alcohol, to the soap is stated not to interfere with the test, since in that case the green fluorescence of the solution is even more pronounced (*cf.* ANALYST, xxx., 313). C. A. M.

On the Behaviour of the most Important Vegetable Oils towards Polarized Light. M. A. Rakusin. (*Chem. Ztg.*, 1906, xxx., 143.)—The author suggests that animal and vegetable oils may be distinguished from mineral oils by means of polarized light, and has compiled the following table :

Oil.	Colour, etc.	Specific Gravity.	Ventzse with a Tube of Mm.			Analyst.[*]	Remarks.
			200	100	50		
A. LIQUID OILS.							
1. *Non-drying Oils.*							
Olive oil (*Ol. olivarum*)	Yellow.	0·9126 (21° C.)	- 0·6	- 0·3			Dark, with
,, (church use) ...	Yellowish-green.	0·9120 (21° C.)	- 0·2			R.	200 mm. tube.
,, (gallipoli) ...	,,	0·9140 (18° C.)	Opaque.	- 0·25			
	,,	0·9134 (18° C.)	- 0·2				
Earth-nut oil	—		- 0·4	—		B.	
,, ...	—		- 0·31			C. L.	7′ to + 24′, with a Laurent.
			to + 1·15				
Croton oil	} Dark yellow.	{ 0·9389 (19° C.)	+ 1·15		+ 3·6	} R.	Benzene is without influence.
,, ...		{ 0·9384 (18° C.)	—	- 8·2	- 4·1		
,, ...			- 63			P.	
Almond oil (sweet) ...	} Light yellow.	{ 0·9160 (20° C.)	- 0·1			} R.	
,, (Persian) ...		{ 0·9130 (23° C.)	< - 0·1				
,, ...	—		- 0·7			B.	
Olive oil			+ 0·6	—		B.	
,, (Provence oil)	} Light yellow.	{ 0·9130 (20° C.)	- 0·2		—	R.	Huil d'olive surfine.
,, ... ,,		{ 0·9120 (21° C.)	+ 0·3			R.	
Rape oil (French) ...	—		2·1			B.	
,, (Japanese) ...	—		1·6			B.	
,, ...	—		0·23			C. L.	5′ to - 10′ with a Laurent.
			to - 0·46				
,, ...	} Light yellow.	{ 0·9136 (15° C.)	- 0·2	—		} R.	
,, (*Ol. rapurum*)		{ 0·9106 (21° C.)	- 0·1				
,, refined) ...		{ 0·9108 (18° C.)	- 0·2				Belgian Co., Odessa.
Castor oil (Italian) ...	} Colourless.	{ 0·9604 (20° C.)	- 8·0	—		} R.	
,, ...		{ 0·9596 (18° C.)	- 8·1		-	W.	
,, ...	—		< - 8·65		-	P.	
,, ...	—		- 10·7				
Mustard oil (Sarepta) ...	Dark yellow.	0·9161 (19° C.)	0·5	- 0·25	—	} R.	J. K. Glitschir, Sarepta.
,, (black) ...	—	0·9144 (22° C.)	Opaque.	0·1			
Sesame oil (cold pressed)	—		- 3·1	—	—		
,, (hot pressed)	—	—	+ 7·2	—	—		
,, 1878 ...	—	—	+ 1·6	—	—	} B.	
,, 1882 ...	—	—	- 3·9	—	—		
,, 1882 ...	—	—	- 9·0	—	—		
,, (Indian) ...	—		- 7·7	—	—		
,, (*Ol. sesame Gallicum*)	} Light yellow.	{ 0·9247 (14° C.)	- 1·9	—	—	} R.	
,, II.		{ 0·9250 (15° C.)	+ 2·1	—	—		
		{ 0·9206 (20° O.	+ 2·3	—	—		
Mustard oil (white) .		—	- 0·13	—	—	C. L.	- 9′ with a Laurent.

[*] B., Bischop ; C. L., Crossley and Le Sueur ; R., Rakusin ; W., Walden.

Oil.	Colour, etc.	Specific Gravity.	Ventzke with a Tube of Mm.			Analyst.	Remarks.
			200	100	50		
A. LIQUID OILS (continued).							
2. *Drying Oils.*							
Cotton-seed oil ...	Light yellow.	0·9220 (22° C.)	− 0·1	...	—	R.	Cotton oil (*Ol. Gossypii*).
Garden cress oil ...	—	—	0	—	...	C. L.	Inactive oil.
Hemp seed oil (raw) ...	Dark green	0·9256 (22° C.)	Opaque.	...	+ 0·1	R.	
Linseed oil (raw) ...	Dark yellow.	0·9314 (21° C.)	,,	+ 0·2	—	R.	Filtered.
,, ...	—		− 0·3	—	...	B.	
,, ...	—	...	+ 0·28	—	...	C. L.	− 6′ with a Laurent.
Cameline oil ...	Dark yellow.	0·9230 (21° C.)	− 0·1	...	—	R.	
Poppy-seed oil	—		0 to 0·17		...	C. L.	0′ to +4 with a Laurent.
,, ,, ...	—		0	—	—	B.	Inactive.
,, ,, ...	Light yellow.	+ 0·9219 (20° C.)	+ 0·1	...		R.	
Niger seed oil ...	—		0 to 0·86	—		C. L.	0° to +18′ with a Laurent.
Walnut oil ...	Almost colourless.	0·9238 (18° C.)	+ 0·15	...	—	R.	
,, ...	—	...	− 0·3	—	...	B.	
"Safflor" oil ...	—		+ 0·17 to 0·66	—	+ ··	C. L.	+ 1′ to + 14′ with a Laurent.
Sunflower oil ...	Light yellow.	0·9195 (22° C.)	+ 0·1	...		R.	
B. SEMI SOLID AND SOLID OILS.							
1. *Viscous Oils.*							
Cocoanut oil ...	White and viscous.	0·9264 (20° C.)	Not examined.	—	—		Crystalline structure.
Cocoanut oil in 50 per cent. benzene solution.	Colourless.	—	+ 0·19 × 2	··	—	R.	
Palm oil ...	Yellow paste.	0·9508 (18° C.)	Not examined.				
Palm oil in 50 per cent. benzene solution.	Light yellow.	—	0·1 × 2	—	—	R.	
2. *Solid Oils.*							
Cocao butter ...	Pale yellow.	0·9702 (20° C.)	Not examined.				
Cocao butter in 50 per cent. benzene solution.	Light yellow.	—	0·1 × 2	—	—	R.	
OTHER OILS.							
Laurel oil ...	Green paste.	0·9335 (19° C.)	Not examined.				
Laurel oil in 25 per cent. ether solution.	Green.	—	—	—	0·9 (× 16)	R.	Tasteless.
Jasmine oil (*Ol. jasmini pinque*).	Almost colourless.	0·9054 (18° C.)	+ 0·9	—	...	R.	
Wild seed oil (*Ol. resedæ pinque*).	Yellow.	0·9122 (18° C.)	+ 0·6	...	—	R.	

A. G. L.

Detection of Artificial Colouring Matter in Fats. A. Olig and J. Tillmans.
(*Zeit. Untersuch. Nahr. Genussm.*, 1906, vol. 11, 94.)—If, during the rendering of a fat, the proteid matter be charred through over-heating, the fat becomes more or less tinted, and imparts a yellow colour to the acetic acid used in the test described by Sprinkmeyer and Wagner (*cf.* ANALYST, 1905, 244). In case a coloration is obtained, the fat should be extracted with alcohol (which is also coloured by the charred proteid matter), and the solution further tested for the presence of coal-tar dyes, etc.

W. P. S.

On the Detection and Determination of Paraffin Wax in Mixtures with Ceresin. F. Ulzer and F. Sommer. (*Chem. Zeitg.*, 1906, xxx., 142.)—Various methods of examining mixtures of paraffin wax and ceresin are discussed. The best appears to be the determination of the refractive index at 90° C., the refractive index of paraffin wax with solidifying points varying from 50° to 60° C. lying between 2·0 and 4·0, whilst the values for ceresins solidifying between 68° C. and 71° C. vary from 11·5 to 13. A sample of German paraffin, however, with a solidifying point of 38° C. gave the high refractive index of 6·81. If only a small quantity of paraffin is present, it may be concentrated by boiling 5 grams of the sample for ten minutes with 100 c.c. of 95 per cent. alcohol, filtering hot, and evaporating, the refractive index of the residue obtained being compared with that of the original. Conversely, if only a small quantity of ceresin is present, 5 grams of the sample are dissolved in 50 c.c. of carbon bisulphide, and 100 c.c. of ether are added. Alcohol is then slowly added, the temperature being kept at 25° C. until a copious precipitate is obtained, which is washed with alcohol and ether, dried, and examined for ceresin. Good indications are also obtained by using Crismer and Motton's method of determining the critical temperature of solution in various solvents, ethyl alcohol being preferred. The critical temperature of solution of various paraffins was found to be, in ethyl alcohol, 155·5° to 158; amyl alcohol, 47° to 54; acetone, 67·5° to 77°; and acetic anhydride, 163 to 176°; whilst some samples of ceresin gave the values 68° to 71°, 174° to 177°, 73·5° to 76°, 95° to 98°, and 191° for the same solvents. A differentiation may also be made by capillarity, ceresin rising much less in filter-paper than does paraffin (6 cm. as against 10 cm. in one hour at 100° C. in the case of two samples compared).

A. G. L.

Determination of Fatty Acids in Textile Soap. Gerhard Krüger. (*Chem. Zeit.*, 1906, xxx., 123.)—Ten grams of the cut-up soap are weighed out into a tared porcelain crucible of 150 c.c. capacity, dissolved in water, and heated with 20 c.c. of dilute (1 : 10) sulphuric acid on a water-bath until the fatty acids have become clear. From 5 to 10 grams of beeswax are then stirred into the fatty acids, and the whole allowed to cool. The solidified fatty cake is then lifted out of the crucible, the acid is poured out, and the cake treated with successive quantities of water until the latter ceases to show an acid reaction. The crucible and fat are then dried for one hour at 70° C., moistened with alcohol and dried for another hour at 100° C., after which they are weighed. The error due to any fatty acid passing into solution in the acid liquid

may be neglected, since even for palm-nut oil soaps it is quite small, whilst cocoanut oil is not used for making textile soaps. A. G. L.

Note on Commercial Oil of Turpentine. W. Vaubel. *(Zeit. öffentl. Chem.,* 1905, xi., 429-432.)—The author recommends the determination of the bromine absorbing power as a means of distinguishing between genuine oil of turpentine and its adulterants. American oil of turpentine was found to have a bromine value of 110 to 115; Russian, 72 to 97; resin "essence" (a product of the distillation of resin), 89. The figures express the grams of bromine required per 100 grams of oil. Russian oil of turpentine is distilled from the roots of the trees, and is an unsatis-factory substitute for the genuine oil. W. P. S.

The Physical Characteristics of Certain Copals. Bottler. *(Chem. Rev. Fett u. Harz. Ind.,* 1906, xiii., 1-5.)—A comparative examination has been made of the characteristics of all the more important copals met with in commerce, many of the results being in tabular form. The physical properties included the appearance of the surface, the colour, transparency, lustre, appearance on fracture, specific gravity, hardness, fusibility and solubility. The specific gravities of the copals in most demand ranged from 1·03 to 1·07 for the substance containing air-bubbles, a higher value being obtained after removal of the air. Speaking generally, the smaller the difference between the densities determined before and after removal of the air, the more valuable the copal. Thus the following differences were observed : Lindi copal, 0·001 ; Zanzibar copal, 0·0015 ; red Angola copal, 0·014 ; Brazil copal, 0·014 ; Cameroon copal, 0·015; Manila copal, 0·059; Hymenæa (South-American) copal, 0·0615; and Kauri copal, 0·064. In the author's opinion the Brazil copal is really a West African and not an American copal. The degree of hardness is an important factor for distinguishing between the different kinds of copals. The hardest is Zanzibar copal, and the other important kinds can be ranged in the following scale : *Hard*—Mozambique, Lindi, red Angola, Sierra Leone (Kiesel), yellow Benguela, white Benguela, Cameroon, and Congo copals ; *Medium*—Manila, white Angola, and Kauri copals ; *Soft*—Sierra Leone (new), Hymenæa, and Brazil copals.

The melting-points of copals range between 90° and 360° C. The following results were obtained by the author : Hymenæa, 95° C. ; Cameroon, 108° C. ; Manila, 112° C. ; Manila (yellow, hard), 135° C. ; Kauri, 126° C. ; Kauri, 140° C. : yellow Benguela, 170° C. ; white Benguela, 175° C. ; Congo, 180° C. ; Sierra Leone, 185° C. ; Kiesel, 220° C. ; white Angola, 245° C. ; Lindi, 246° C. ; Zanzibar, (*a*) 259° C., (*b*) 265° C. ; and red Angola, 305° C. The solvents tried included chlorhydrin, terpineol, and carbon tetrachloride, in addition to the older solvents. A rapid method of dissolving copals (*e.g.,* West African varieties) consists in heating them for forty-eight hours at 100° C., mixing them with sand or glass powder, digesting the mixture for twenty-four hours with anhydrous ether, and finally adding an equal quantity of hot alcohol. Turpentine oil has usually only a solvent action on copals when it contains ozone. The different copals can be arranged in the following order as regards their solubility in the solvents most commonly employed : White Angola,

Manila, Kauri, Brazil, Congo, Sierra Leone, yellow Benguela, red Angola, white Benguela, Kiesel, Cameroon, Lindi, and Zanzibar copals.   C. A. M.

Recovery of Iodine from the Residues obtained in Hübl's Method.
A. Olig and J. Tillmans. (*Zeits. Untersuch. Nahr. Genussm.*, 1906, vol. 11, 95-97.)
The solutions obtained after the final titration in determinations of the iodine value of fats by Hübl's method are collected until a good quantity is obtained. After removing the chloroform by means of a separating funnel, the aqueous portion is rendered strongly alkaline with sodium hydroxide, and evaporated as far as possible. The mercury compounds (oxide, basic carbonate, and some metal) are filtered off, washed, and the filtrate again evaporated to dryness and ignited. A little mercury will still be present, and care must be taken during the ignition. The residue is dissolved in water, filtered from any insoluble matter, and the solution then rendered strongly acid with hydrochloric acid. The mixture is now warmed, and a concentrated potassium bichromate solution is added until all the iodine has been precipitated. The liquid is then decanted, the iodine is washed with a small quantity of water, and distilled from a retort in a current of steam. The distilled iodine is collected in a well-cooled receiver, from which it may be readily removed in its wet state, and then dried or sublimed.   W. P. S.

Notes on the Determination of Calorific Values by means of the Bomb.
D. Aufhäuser. (*Zeits. angew. Chem.*, 1906, xix., 89.)—In order to make the temperature corrections as small as possible, the water used should be initially as much below the normal temperature as it is finally above it. The temperature of the water in the calorimeter may be most conveniently adjusted for this purpose by putting colder water into the calorimeter, placing the bomb in position, starting the stirrer, and then warming the whole to the required temperature by means of a small electric heater, preferably a cylindrical electrical lamp. The lamp should be wetted before it is plunged into the water in order to obviate the error due to adhering water when it is taken out.   A. G. L.

The Volumetric Determination of Organic Hydrosulphides and Thio Acids.
P. Klason and T. Carlson. (*Berichte*, 1906, xxxix., 738-742.)—Titration of organic hydrosulphides with an aqueous solution of iodine gives under suitable conditions quantitative results in accordance with the equation :

$$2R.SH + I_2 = R_2S_2 + 2HI.$$
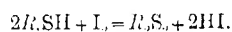
Thiocyanic acid, however, does not react in this way. The presence of bicarbonate is not only unnecessary, but may lead to further oxidation. The weighed quantity of the hydrosulphide is dissolved in alcohol and titrated with N-iodine solution until a faint yellow colour appears. It is essential that there shall be sufficient alcohol present to keep the bisulphide formed in solution, since otherwise it too can absorb iodine, and the results will be too high. The results of test experiments with different classes of thio compounds, such as p-thiocresol, methyl and ethyl hydrosulphides,

thioglycollic, and thioacetic acid, show that the method is capable of great accuracy. Rosenheim and Davidson found that the reaction between thioglycollic acid and iodine in sodium bicarbonate solution gave a quantitative yield of dithioglycollic acid ; but the author finds that the results thus obtained are not constant, and are invariably too high owing to further oxidation with the formation of thioacetic acid. This latter acid, too, also undergoes further oxidation in a bicarbonate solution, acetyl-bisulphide being produced.

Aromatic hydrosulphides—*e.g.*, thiophenol, β-thionaphthol, and *p*-thiocresol—are so strongly acid that they form salts with alkalies in neutral solutions, and can therefore be titrated with standard alkali solution, phenolphthalein being used as indicator. The more carbon the molecule of the compound contains, the greater the accuracy of the results. With alipathic hydrosulphides the end reaction is not sharp, and thioglycollic acid cannot be titrated with alkali either in aqueous or alcoholic solution. C. A. M.

On Quantitative Determination by Means of the Immersion Refractometer. H. Matthes.

(Chem. Ztg., 1906, xxx., 101.)—The author severely criticises some applications of the use of the immersion refractometer made by Wagner *(Ztschr. öffentl. Chem., 1905, xi., 404)*, especially in the case of sugar analysis. For legitimate uses of the instrument, such as the control of beer, wine, etc., prepared in the same way and under the same conditions, and the control of the strength of standard solutions, he refers to his own work *(Ztschr. analyt. Chem., 1904, xliii., 83)*.
A. G. L.

Simplified Ultimate Organic Analysis for Scientific Purposes. M. Dennstedt.

(Chem. Zeit. Rep., 1905, xxix., 390.)—In the use of the simplified method (see ANALYST, xxx., 135) of the author a difficulty arises from the fact that, as some substances require different treatment in the combustion, these must be burnt in succession. The author now suggests some improvements.

The chief point of the "quick" method is that the boat containing the sub-stance is not placed directly in the combustion tube, but in a narrow, hard glass tube, which may take any of three forms : (1) The form open at both ends, *a*, Fig. 1:

Fig. 1.

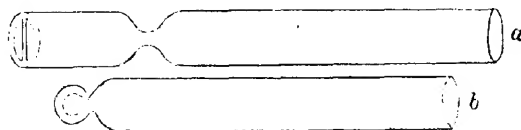(2) that with the hinder end closed, *b*, Fig. 1; or (3) that with a double current of oxygen, Fig. 2.

The last named is fitted with a capillary and a bubble counting arrangement through which the oxygen enters the inside of the tube. A T-piece of somewhat wider bore fits over the capillary, and is provided with a cork to fit into the main combustion tube. The main current of oxygen passes through the calcium chloride

tube and the side tube of the T-piece. The bubbling apparatus and the calcium chloride tube are each connected to the ordinary drying apparatus by rubber tubing,

Fig. 2.

which allows the tube to be withdrawn with one hand for introduction of the boat, etc.

Form a is suitable for the combustion of substances which decompose slowly, with formation of much carbon difficult to burn—e.g., sugar, albumin; form b is for use with easily volatile or moderately volatile substances, which do not give a separation of difficultly combustible carbon—e.g., alcohols, benzol, aniline, etc.

The third kind of tube is serviceable for all substances without exception. The regulation of the combustion is especially easy, as this can be effected not only by the flame, but also by increasing or diminishing the rate of the inner current of oxygen.

The tubes can be obtained from Emil Dittmar and Vierth, Hamburg.

E. K. H.

INORGANIC ANALYSIS.

The Estimation of Opalescent Silver Chloride Precipitates. Roger Clark Wells. (*Amer. Chem. Journ.*, 1906, vol. 35, 99.) A number of small precautions are described, which must be used in connection with the nephelometer (ANALYST, 1905, xxix., 203). It is found that ground-glass standards are to be preferred, and that for every concentration a suitable solution and excess of precipitant are required. It is also shown that the presence of electrolytes both augments the maximum opalescence and hastens its disappearance through coagulation. The best procedures in a number of special cases are also described.   A. G. L.

The Volumetric Determination of Copper. G. Denigès. (*Ann. de Chim. anal.*, 1906, vol. 11, pp. 10-12.)—Ammoniacal solutions of cupric salts form double colourless compounds with alkali cyanides, thus:

$$CuSO_4 + 4NH_4CN = (NH_4)_2SO_4 + Cu(CN)_2.2(NH_4)CN.$$
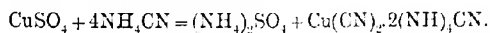
The double cyanide thus formed is very stable, but gives up a portion of its cyanogen on treatment with silver nitrate, the amount varying, e.g., with the degree of alkalinity of the liquid. The author has found that when the quantity of the copper salts taken contains from 1 to 50 mgms. of the metal, whilst 20 c.c. of $\frac{N}{5}$ potassium cyanide solution and 2·6 grams of ammonia are used, the total amount

of liquid being 120 c.c., each cgm. of copper gives up to the silver an amount of cyanogen equal to 2·5 c.c. of the potassium cyanide solution, or in other words each c.c. of cyanide solution is equivalent to 4 mgms. of copper. In making a determination, a quantity v of the solution of the cupric salt containing not more than 50 mgms. of copper is treated with a volume v' of ammonia solution containing 2·6 grams of ammonia, and with 20 c.c. of $\frac{N}{10}$ potassium cyanide solution (standardized on the silver nitrate solution). Then, after the addition of 1 c.c. of a 10 per cent. solution of potassium iodide, and $99 - (v + v')$ c.c. of water, the liquid is titrated with $\frac{N}{10}$ silver nitrate until there is a faint but persistent turbidity. If n c.c. be used, the value $(20 - n)$ c.c. represents the cyanide taken up by the silver, and $(20 - n) \times 0·004$ gram gives the amount of metallic copper in the amount, v, of solution taken. In order to obtain concordant results it is necessary that the volume of $v + v'$ should not exceed 100. In testing cupric sulphate by this method the presence of zinc does not interfere with the results unless it amounts to 40 to 50 per cent. of the quantity of the copper salt.

Volumetric Determination of Copper and Mercury in Admixture with Each Other.— A quantity v (not exceeding 100 c.c.) of the solution, which should not contain more than 0·5 gram of mercury and 0·1 gram of copper, is treated with 5 c.c. of hydrochloric acid (specific gravity 1·18), and 5 c.c. of a solution (1 : 5) of cystallized sodium phosphite, and boiled for five minutes with continual agitation, after which it is filtered, and the filtrate and wastings made up to 150 c.c. The copper is then determined in 75 c.c. of this liquid in the manner described above, with the difference that it is necessary to add a constant of 0·8 c.c. to the volume of silver nitrate, n, consumed, to make up for the modification in the reaction caused by the added salts. The precipitate (containing the mercury) left on the filter is detached with the aid of a fine jet, and treated with 5 c.c. of water, 5 c.c. of hydrochloric acid, and 0·25 gram of potassium chlorate, the whole being heated until solution is complete, and the liquid then cooled and made up to 100 c.c. An aliquot portion (a c.c.) of the solution is now mixed with 12 c.c. of ammonia solution (25° Bé., S.G. 0·9), 10 c.c. of $\frac{N}{10}$ potassium cyanide solution, $100 - n$ c.c. of water, and 1 c.c. of a 10 per cent. solution of potassium iodide, and titrated with $\frac{N}{10}$ silver nitrate solution. If q c.c. be used, $(10 - q) = n$ represents the amount of cyanogen in terms of $\frac{N}{10}$ potassium cyanide solution given up by the mercury to the silver. This figure must be corrected by multiplying by the factor 0·96 if it lies between 0 and 5·5, or by the factor 1·04 and subtraction of 0·45 of the product if it lies between 5·5 and 9·5. The corrected value, c, multiplied by 0·02 gram (one ten-thousandth of the atomic weight of mercury) gives the quantity of that metal in the amount of solution, a, taken.   C. A. M.

The Separation of Metals of the Arsenic Group. O. Materne. (*Bull. Soc. Chim. Belg.*, 1905, xix., 241.)—The mixed sulphides of arsenic, antimony, and tin are boiled with a 2 per cent. solution of borax containing some ammonium chloride (amount not stated), and the liquid allowed to cool and filtered. The filtrate contains the arsenic, which is precipitated by means of tartaric acid. The residue of the two other sulphides is treated with a boiling 5 per cent. solution of sodium carbonate (containing some ammonium chloride), which dissolves the antimony sulphide and

leaves the stannous sulphide. On treating the filtrate with tartaric acid the antimony sulphide is re-precipitated, whilst the residue of stannous sulphide can be brought into solution by means of a 10 per cent. solution of sodium hydroxide.

C. A. M.

Determination of Carbon in Steel by Direct Ignition with Red Lead.
Charles Morris Johnson. (*Proc. Eng. Soc. West. Pennsylvania*, 1906, xxi., 586.)— The author has found that for molybdenum and chromium steels the ordinary potassium cupric chloride method of determining carbon gives very discordant results, as the carbide obtained appears to oxidize rapidly if exposed to air, or, in some cases at least, to acid. He therefore burns such steels directly with red lead in a current of oxygen, the resulting carbon dioxide being absorbed in barium hydrate, and the barium carbonate formed filtered off and weighed. The baryta is contained in two large test-tubes, through which the carbon dioxide bubbles. The steel used should pass a 20-mesh sieve and be retained by a 30-mesh, or else it may be in the form of fine drillings. For high carbon steels, 0·5 to 1 gram is taken; for low carbon steels, 2 or 3 grams may be used. The sample is placed in a weighing bottle with 4 grams of red lead, and well mixed by shaking; the mixture is then transferred to a porcelain boat and covered over with asbestos, which prevents creeping. The highest heat obtainable should be used for the combustion. Old boats may be cleaned with nitric acid. A combustion by this method takes in all only seventy-five minutes from start to reporting, and results obtained on ordinary steels check exceedingly well with those given by the usual method. A. G. L.

Determination of Sulphur in Roasted Zinciferous Ores and Similar Materials. G. Lunge and R. Stierlin. (*Zeits. angew. Chem.*, 1906, xix., 21.)—
The authors show that the Watson-Lunge method is not applicable to materials containing zinc, and recommend the following: Exactly 2 grams of sodium bicarbonate, the alkali content of which is accurately determined, is mixed in a small nickel crucible with 3·206 grams of the finely powdered sample and 2 grams of potassium chlorate. The crucible is covered and heated for one hour, for the greater part of the time very gently, but finally to dull redness, without, however, allowing the mixture to fuse. The mixture is then extracted with water to which 25 c.c. of sodium chloride solution, absolutely neutral and free from magnesium salts, have been added. The whole is boiled until sodium chloride commences to separate out, when the insoluble residue is filtered off and washed with sodium chloride solution (to prevent iron oxide from passing through the filter). The filtrate is then titrated with hydrochloric acid, using methyl orange as indicator. The difference between the alkali value of the sodium bicarbonate taken and that found corresponds to the sulphur. If more than 6 per cent. of sulphur is present, only 1·603 grams of substance should be taken, and 2 grams of ferric oxide added, to prevent fusion of the mixture. A. G. L.

Titanium Chloride in Volumetric Analysis. E. Knecht and E. Hibbert.
(*Chem. Zeit. Rep.*, 1905, xxix., 380.)—The authors have successfully used the strong

reducing action of titanium chloride for the volumetric analysis of other substances, especially coloured organic compounds which form colourless "leuco-" bodies. This is usually effected by the addition of 2 atoms of hydrogen to the molecule. The colouring matter acts as its own indicator in the titration, as the end of the reaction is marked by the solution becoming colourless. The experiments must be conducted in absence of air, owing to the ease with which the "leuco-" bodies are oxidized. The authors also succeeded in accurately estimating inorganic substances by the same reagent. E. K. H.

Analysis of Incandescence Mantles. T. B. Stillman. (*Chem. Zeit.*, 1906, xxx., 60.)—The following scheme of procedure is given : Five mantles are burnt off, broken intó small pieces, weighed, and evaporated with sulphuric acid in a platinum basin to dryness. This digestion is repeated four times. When cold, the mass is extracted with cold water, and the solution filtered, if necessary. The residue, if any, is fused with potassium hydrogen sulphate, diluted with water, and added to the main solution. Ammonium sulphide is now added in slight excess, and the precipitate collected on a filter and washed with water containing ammonium sulphide. The filtrate contains the calcium and magnesium, which are separated in the usual manner, after boiling the solution to drive off hydrogen sulphide, and filtering to remove separated sulphur. The precipitate contains the hydroxides of cerium, thorium, lanthanum, zirconium, aluminium, didymium, and yttrium. It is dissolved in hydrochloric acid, diluted with water, boiled; a dilute solution of sodium thiosulphate is added, the whole boiled for one hour, then allowed to stand for twelve hours and filtered, giving precipitate "A" and filtrate "B."

Precipitate "A" contains the oxides of thorium, zirconium, and aluminium. These are dissolved in hydrochloric acid filtered from precipitated sulphates; the latter are dried, ignited, fused with potassium hydrogen sulphate; the melt dissolved in cold water, precipitated with ammonia, filtered, and the precipitate dissolved in hydrochloric acid and added to the main hydrochloric acid solution. The latter is treated with an excess of sodium thiosulphate, boiled, filtered, treated with ammonia in slight excess, again filtered, and washed with water. The precipitate is dissolved in hydrochloric acid, supersaturated with oxalic acid, boiled for five minutes, allowed to stand for twelve hours, and filtered.

Precipitate. Wash with cold water, dry, ignite, and weigh as ThO_2. Gives no absorption spectrum.	Filtrate. Treat with excess of sodium hydroxide, boil for ten minutes, filter, and wash with hot water.	
	Precipitate. Dry, ignite, and weigh as ZrO_2. Gives no absorption spectrum.	Filtrate. Acidify with hydrochloric acid, render feebly alkaline with ammonia; boil, filter, wash, and weigh as Al_2O_3. No absorption spectrum.
ThO_2.	ZrO_2.	Al_2O_3.

Filtrate "B" contains the oxides of cerium, yttrium, lanthanum, didymium, and thorium. The solution is rendered alkaline with ammonia, filtered, washed with

cold water, the precipitate dissolved in hydrochloric acid, and the solution treated with dilute sodium thiosulphate solution to precipitate any thoria present. Any precipitate obtained is dissolved in hydrochloric acid and added to the hydrochloric acid solution of precipitate "A." The filtrate is precipitated with ammonia, filtered, washed, the precipitate dissolved in sulphuric acid; the excess of the latter is ignited, and the residue dissolved in cold water. The solution is now treated with a saturated solution of potassium sulphate, and the precipitate collected on a filter after standing for four hours, and washed with a solution of potassium sulphate.

Precipitate. Dissolve in dilute hydrochloric acid, add oxalic acid, filter, dry, and ignite. Dissolve the residue in hydrochloric acid, precipitate with sodium hydroxide, saturate with chlorine gas, filter, and wash well.

Filtrate. Add a dilute solution of sodium hydroxide; filter off the precipitate, wash, dry, and weigh as Y_2O_3. Gives no absorption spectrum.

Precipitate. Dry, ignite, and weigh as CeO_2. Gives no absorption spectrum.

Filtrate. Acidify with hydrochloric acid, boil, precipitate with oxalic acid, filter, wash, dry, and ignite. The residue is dissolved in nitric acid, and divided into two parts:

Test for Di with the spectroscope. A dark band shows that Di is present.

Add ammonium acetate, then ammonia, and filter. Treat the precipitate with solid iodine. Lathanum gives a blue colour, but no spectrum.

CeO_2.

Di_2O_4.

La_2O_3.

Y_2O_3.

The didymium may consist of praseodymium and neodymium; the salts of the former are green and of the latter rose-red.

W. P. S.

The Separation of Iodine from Chlorine and Bromine by Means of Hydrogen Peroxide. J. Jannasch and F. Zimmermann. (*Berichte*, 1906, xxxix., 196, 197.)—The aqueous solution of the mixed halogens (120 to 150 c.c.) is treated with 15 c.c. of glacial acetic acid, and 3 c.c. of hydrogen peroxide (30 per cent.), which effects a quantitive separation of the iodine from the chlorine and bromine. The iodine thus liberated is distilled by means of a current of steam into three connected vessels containing respectively (a) 10 grams of hydrazine sulphate, and 10 c.c. of ammonium hydroxide in 80 to 100 c.c. of water, and (b) and (c) 0·5 gram of hydrazine sulphate, and 2 c.c. of ammonium hydroxide in 25 c.c. of water. After the whole of the iodine has passed over, the contents of the absorption vessels are cooled, mixed, and acidified with 30 to 40 c.c. of strong sulphuric acid, and the iodine determined as silver iodide.

C. A. M.

The Detection and Determination of Chlorate in Sodium Nitrate.
L. Grimbert. *(Journ. Pharm. Chim.*, 1906, xxiii., 98-100.) — A few c.c. of a solution of the sodium nitrate are shaken with one drop of aniline, and a little strong sulphuric acid then poured down the side of the tube. In the presence of a chlorate an intense blue zone appears at the junction of the liquids. For the determination of the chlorate a given weight of the sodium nitrate is ignited with a little cane sugar to effect reduction, the mass extracted with water, and the chloride determined by titration in the usual manner. In this way the author found a sample of sodium nitrate to contain 0·692 per cent. of sodium chlorate. Three other samples of sodium nitrate free from chloride also contained chlorate, but different samples of potassium nitrate examined were found to be quite pure. C. A. M.

Use of the Electric Furnace for Burning Magnesium Phosphate Precipitates. F. Haussding. *(Chem. Zeit.,* 1906, xxx., 60, 61.)—The construction of the furnace is shown in the illustration. The crucible containing the precipitate of ammonium magnesium phosphate rests on a quartz-glass triangle or on a piece of platinum foil placed on the bottom of the furnace. The lid of the furnace is also covered with platinum foil. After passing a current of 1·5 ampères at a pressure of 220 volts through the furnace for twenty minutes, it is ready for use. Only two minutes' heating are required to obtain a completely white residue of magnesium pyrophosphate, and there is no danger of the high temperature causing loss of phosphoric acid. The use of the furnace does away with the injurious action of ordinary gas-flames on the platinum crucibles. W. P. S.
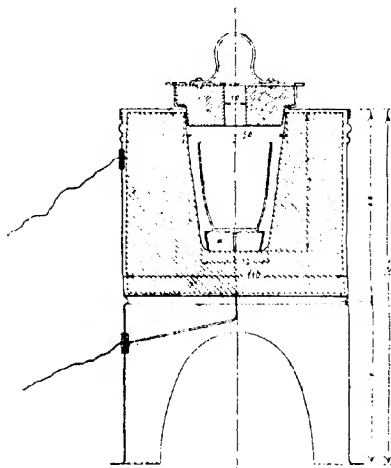
The Determination of Carbon Monoxide in Air. A. Levy and A. Pécoul. *Comptes Rendus,* 1906, cxlii., 162.)—The method is based upon the fact, recorded by Gautier, that carbon monoxide, even when only present in traces in air, reduces iodic anhydride, and also on the colorimetric determination in a chloroform solution of the iodine thus liberated. Acetylene has a similar reducing action, but to a much smaller extent. Thus, air containing 4 parts per 10,000 of acetylene causes only a very slight reduction of the iodic anhydride, whereas with 1 part of carbon monoxide in 10,000 a large amount of iodine is liberated. Hence in testing ordinary air for carbon monoxide no special precautions are necessary, but in the case of industrial gas-products any acetylene, hydrogen sulphide, etc., must be absorbed

before making a determination. The most accurate results are obtained by using a solution of potassium hydroxide for the absorption of the iodine.   C. A. M.

Determination of Water in Superphosphates and in Silicofluorides.
Ludwig Schucht. (*Zeits. angew. Chem.*, 1906, xix., 183.)—To determine *moisture*, as distinct from chemically combined water, in *superphosphate*, 2 grams of the sample are rubbed up in a glass dish with 20 c.c. of absolute alcohol. After one hour the liquid is decanted through a weighed filter-paper; the insoluble material is brought on to the filter with more alcohol, washed with ether, dried at 40° C., and weighed. The filtrate is evaporated to dryness, and the residue dried at 120 C. to constant weight. The weighings must be made as quickly as possible. The difference between the original 2 grams and the sum of the two residues gives the moisture. For the determination of *free acid*, the author recommends the use of his oxalate method, and answers some objections which have been brought against it.

To determine the free acid in commercial *silico-fluoric acid*, 50 c.c. are weighed out, diluted with water to 1 litre, and 50 c.c. of this solution titrated hot with $\frac{N}{2}$ sodium hydroxide, using phenolphthalein as indicator. If free hydrofluoric acid is also present, the total acid is determined in this way, and the precipitate produced by potassium chloride and ethyl alcohol by Stolba's method is also weighed. The precipitate may also be titrated with sodium hydroxide.

In the analysis of commercial *sodium silico-fluoride*, *moisture* is determined by heating 2 grams of the substance for three hours at 100 C. in a current of dry air which has to bubble through $\frac{N}{2}$ sodium hydroxide after passing over the substance, any volatilized acid being thus retained and allowed for. To determine *free acid*, 3 grams of the sample are moistened with methyl orange in a glass dish, and titrated with $\frac{N}{2}$ sodium hydroxide. To determine the sodium silico-fluoride, 3 grams of the sample are dissolved in 450 c.c. of water, and the solution is titrated hot with $\frac{N}{2}$ sodium hydroxide, using phenolphthalein as indicator. The free acid previously found must be deducted from the result, and the proportion of sample to water should always be that stated, otherwise errors due to hydrolysis will be made.   A. G. L.

Determination of Available Plant Food in Soil by Use of Weak Acid Solvents. A. D. Hall and A. Amos. (*Proc. Chem. Soc.*, 1906, xxii., 11.)—Repeated extraction, with water charged with carbon dioxide or with a 1 per cent. solution of citric acid, of soils of known history has shown that the first extraction does not remove the whole of the soluble phosphates, the reaction being a reversible one. With carbon dioxide and water the position of equilibrium is approximately constant for successive extractions, but with dilute acetic acid the amount of phosphoric acid dissolved falls for the first four or five extractions, then becoming nearly constant. No support is found for the theory that all soils establish in the soil-water a solution of phosphoric acid of approximately the same composition, and independent of the fertilizers the soil receives.   W. H. S.

Mechanical Analysis of Soils. J. A. Murray. (*Chem. News*, 1906, vol. 93, p. 40.)—The author has worked out the following scheme for the mechanical analysis

of soils : Five grams of the air-dried fine soil (passed through a 100-mesh sieve) were disintegrated in weak ammonia solution and allowed to stand for fifteen minutes, after which the water containing the finer material in suspension was poured off. The coarser material was then introduced into a 200 c.c. Erlenmeyer flask, which was filled with water and attached by a rubber joint to a wide glass-tube of exactly the same diameter as the neck of the flask, from which the flange had previously been removed. The tube used was 147 cm. long and 2·3 cm. internal diameter. Water was next poured gently down the side of the tube so as to fill it, after which it was closed by a cork and inverted in a large glass basin full of water. The cork was then immediately removed and a small weighed porcelain dish placed under the open end of the tube under the water. The particles descending the tube were collected in a series of fractions, the first porcelain dish being removed and another one substituted five minutes after the first particle had reached the bottom, the second dish being removed after another ten minutes, and the third after another twenty minutes (or else, after another twenty-five minutes, the times as given not corresponding exactly with each other). Nearly the whole of the remainder of the material was deposited in another hour. This last fraction was returned to the beaker containing the quantity of fine material originally poured off, well mixed with it, and the whole then placed in the flask and allowed to fall through the tube as before, the same water being used so as to avoid loss of material. In this way three more fractions were collected, after one, three, and seven hours respectively. The liquid remaining in the flask and tube was then measured and an aliquot part evaporated to dryness so as to give a seventh and last fraction of finest material. The other fractions collected were also dried and weighed. The preliminary separation into finer and coarser material is necessary to prevent some of the fine particles being dragged down with the coarse material. The method enables a soil to be separated into a number of fractions containing particles of nearly uniform size ; duplicate analyses made by it are in good agreement with each other.　　　　　A. G. L.

A Rapid Method for the Determination of Moisture in Fuels, especially Coal. E. Graefe. (*Braunkohle*, 1906, iv., 581 ; through *Chem. Zeit. Rep,.* 1906, xxx., 23.)—Ten grams of the coal are heated with 50 c.c. of solar oil or petroleum in a 75 c.c. distilling flask until 25 c.c. of oil have been distilled off, which should require about five minutes. The distillate is caught in a 25 c.c. measuring cylinder, the amount of condensed water being read off directly ; each $\frac{1}{10}$ c.c. corresponds to 1 per cent. of moisture in the coal. The neck of the distilling flask should only reach a short distance above the side-tube, and a narrow condenser tube (above 5 mm. diameter) should be used. The method is stated to give serviceable results.

A. G. L.

Standardization of Chemical Disinfectants. (*Chem. Trade Journ.*, 1906, xxxviii., 4.)—The large variety of these now on the market renders desirable their classification according to their efficiency, and since they are sold for germicidal purposes, any comparison should be on this basis. The need for standardization is emphasized by the following table, taken from the *Public Health Engineer*.

Sample.	Carbolic Acid Coefficient.	Price per Gallon, or 10·5 lbs.			Cost of Disinfectant equivalent to 1 Gallon of Carbolic Acid.		
		£	s.	d.	£	s.	d.
A.	0·02	0	3	6	8	15	0
B.	0·30	0	5	6	0	18	4
C.	8·00	0	4	0	0	0	6
D.	1·00	0	1	0	0	1	0
E.	2·50	0	8	0	0	3	2
F.	1 40	0	2	6	0	1	9
G.	0·30	7	17	6	26	5	0
H.	0·10	0	18	9	9	7	6
I.	0·10	0	15	0	7	10	0
J.	0·90	0	7	6	0	8	4
K.	2·50	0	3	6	0	1	5
L.	0·03	2	0	0	66	13	4
M.	11·00	0	4	0	0	0	4

W. H. S.

Determination of Turbidity of Water. J. F. Liverseege. (*Journ. Soc. Chem. Ind.*, 1906, xxv., 45.)—Test type as used by oculists, mounted on a board and attached to a cord running on a pulley, is viewed through a 2-foot tube, filled with the water under examination, and placed with its end about 6 inches from the type, which is raised or lowered till a set is found that can be easily read. The turbidity figure is obtained by subtracting 2·5 feet from the normal range in feet for the particular type, and is recorded as "turbidity expressed in feet of distance required to read standard type." If a water is so turbid that 2 feet of it obscures the type entirely, a 1-foot tube may be used, still reading at 2·5 feet from the type, but the results cannot be calculated from one tube to the other. W. H. S.

Filtration of Finely Divided Precipitates. C. S. Palmer. (*Chem. Zeit. Rep.*, 1905, xxix., 342.)—The author proposes to add 1 or 2 drops of albumen to the liquid to be filtered, and, after stirring, to quickly raise to boiling. The coagulated albumen enables the precipitate to be easily filtered, washed, and burnt. The trace of ash from the albumen is quite negligible. E. K. H.

APPARATUS.

A Form of Burette for avoiding Errors in Titration at the Boiling-point. H. Göckel. (*Chem. Zeit.*, 1905, xxix., 1208.) A modification of Koninck's burette, in which the exit-tube comes out at right angles to the main tube. In the present type the side tube is not horizontal, but curves up somewhat and then down again. This avoids the necessity of placing the burette at a high level. The burette can be obtained from Dr. H. Göckel, Berlin, W. E. K. H.

Heating under Reduced Pressure by the Aid of an Electric Oven.
E. Haagn. (*Chem. Zeit.*, 1905, xxix., 1209.)—The accompanying figure shows a
very useful form of electric oven, furnished with an arrangement for giving a partial
vacuum. The bottom portion of the appa-
ratus is made with a double wall, between
which water circulates, being admitted by
the aperture B, and running off by aperture
A. In consequence of this cooling, the top
can be safely provided with a rubber fitting,
which insures an air-tight joint. The oven is
exhausted by means of the tube C, connected
to a water-pump.
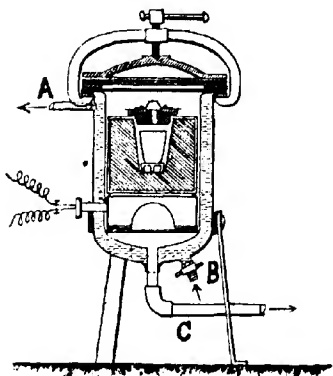
The oven itself is a modification of that
designed by W. C. Heraeus, of Hanover, but,
in contrast to the earlier models, the heating
resistance is within the mass of the oven
body. This gives greater heat economy in
working, and causes the highest temperature
to be more quickly attained. A temperature
of 1100° C. can be obtained, and this is reached in about twenty to twenty-five
minutes. About ½ kilowatt is used.

For ordinary purposes a good water-pump gives a sufficiently reduced pressure;
but, of course, any desired reduction can be obtained by the ordinary means. The
advantages of heating in a partial vacuum are often very great. Thus marble, which
requires a good half-hour in a gas furnace for complete conversion to lime, is, in the
present apparatus, completely converted in three minutes after the full temperature
is attained. By first exhausting and then admitting any gas, it is easy to use this
apparatus for heating substances in an atmosphere of any desired gas.

The advantages of electric heating are also obtained by this oven. The influence
of gas flames on platinum crucibles is especially bad, and the avoidance of this evil
is almost a sufficient recommendation.   E. K. H.

An Improved Pattern of Gooch Crucible. H. Vollers. (*Chem. Zeit.*, 1905,
xxix., 1088.)—The principle of this form of crucible is clearly
indicated in the accompanying figure. In place of the usual
perforated bottom, there is a raised cylinder with the holes
passing through the wall, the direction of the holes being
parallel to the bottom.

By this device the author claims to have removed the defect
shown by an ordinary Gooch crucible, that the pores get blocked
up by the asbestos; the asbestos can be pressed down very
firmly, and, if the filtration is then too slow, some of the
holes, usually only a few, can be cleared by means of a bent
needle.

The crucible is supplied by the firm of C. Gerhardt, Bonn a. Rh.   E. K. H.

A Constant Temperature Bath for Low Temperatures.   A. Given.

(*Journ. Amer. Chem. Soc.*, 1905, xxvii., 1519.)—The bath shown in Fig. 1 was designed originally to keep pyknometers at a constant temperature of 15·6° C.; but it has since been found to work well at other moderately low temperatures. In principle it consists essentially of a bath of distilled water, in which the greater part of the pyknometer is immersed, and which is cooled by an ice-box, and heated by a Bunsen burner (not shown) fitted with a gas-regulator. The bath itself is double-walled, the space between the outer galvanized iron wall and the inner copper wall being packed with asbestos. The ice-box I is of copper, and fitted with a wooden cover. It is raised 1½ inches above the bath, so as to
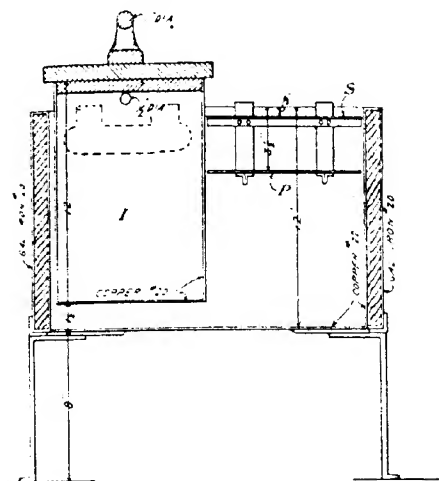
Fig. 1.

leave space for an overflow-pipe, and it extends to within 1½ inches from the bottom of the bath. A gentle current of air is introduced close to the bottom of the ice-box, and serves to stir the water in the outer bath. The pyknometers stand on the perforated shelf I', supported on hangers, which also carry the narrow shelf S for the thermometer and gas-regulator. This last is shown in Fig. 2, and consists of a large bulb, A, 5 inches long and 1 inch in diameter, filled with methyl alcohol (toluol might be even better). M represents the mercury seal, R being a rod of glass to strengthen the apparatus. The gas enters at I and leaves at O; at P there is a hole for the pilot-flame supply.

In using the bath, the pyknometers are first of all cooled to about 14° C., and then only placed in the bath, in which they may remain for any reasonable time. A bath, 18 inches square and 12 inches deep, consumes about 50 pounds of ice in seven hours in the hottest weather, but less than 1 pound of ice in it will keep the temperature of the bath constant.

Fig. 2.

A. G. L.

A Modification of Gintl's Pyknometer. M. Raukusin. *(Chem. Zeit.,* 190⁵, xxix., 1087.)—The author brings forward a modified form of apparatus, the design of which is seen in the accompanying figure.

The sample of fat is contained in the cylinder *a*, which in this form is open at *both* ends. The lower end of this pyknometer tube is ground to f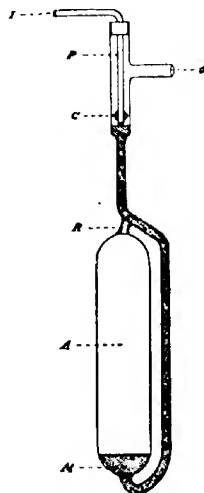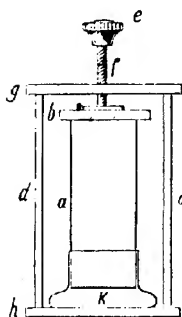it the glass cap *k*, which is ground on the inside, and thus a tight joint closes the tube. On the upper edge of the pyknometer tube a glass cover, *b*, is laid, which closes the tube tightly through receiving the wall of the tube in a small annular canal.

The apparatus is used as follows: The three portions of the instrument are carefully cleaned and dried. The tube *a* is then placed in the cap *k*, and filled with the melted fat. The cover *b* is then laid on the tube, so that the wall of the tube fits exactly with the canal in the cover. The whole instrument is then placed in a metal clamp, shown in the figure, and the excess of fat removed by pressure from the screw *f*, and the instrument then washed with petroleum ether and cleaned with chamois leather.

The fat can be removed from the cylinder by a glass rod, the last traces being got rid of with ether, etc.   E. K. H.

A New Crucible Triangle.   A. Kette. *(Chem. Zeit.,* 1905, xxix., 1208.)—The author points out the failings of the ordinary pipeclay triangle and the platinum triangle. In particular all forms suffer from the defect that the flame is broken on the bottom of the crucible, and its further heating power is thus lost. To remedy this defect, the author brings forward the arrangement shown in the figure.

The crucible rests on the angles of the three prisms, and the flame touches only fire-resisting material.   The ring surrounding these pieces can be tightened and loosened by means of the small screw, and the opening thus altered to fit various-sized crucibles.   Finally, the effective heating of any given flame is much increased, as very little of its power is lost.

The author states that a platinum crucible can be easily and quickly raised to a temperature of 1300° C.. This apparatus can be obtained from the firm of Bender and Hobein, Munich.   E. K. H.
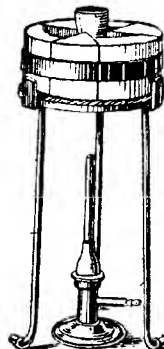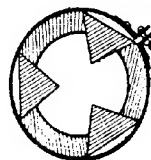
A New Vacuum Filter for Laboratory and Domestic Use and a wholly Novel Method of Cleaning the Filtering Material. (*Zeits. angew. Chem.*, 1906, xix., 95.)—In the vacuum filter described the filtering material may be easily cleaned by evacuating the upper part of the apparatus by means of the pump *p*, as shown in Fig. 1, air being sucked in through the opening F below the filter. As soon as the filter is thoroughly clean, the liquid in A will become filled with small air-bubbles. The air admitted through F may be previously sterilized in any convenient way. Fig. 2 shows the normal way of working the apparatus as a filter. It may be obtained of the following firms: Warmbrünn, Quilitz and Co., Berlin, N.W., Haidestrasse 55 to 57; Albert Dettloff, Berlin, N.W., Luisenstrasse 59; Franz Hugershoff, Leipzig.
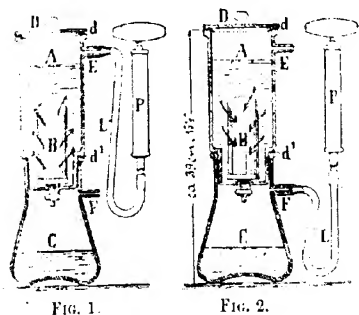
A. G. L.

FIG. 1.   FIG. 2.

Apparatus for Continuous Extraction of Liquids with Ether, Benzene, or other Solvent. R. S. Bowman. (*Proc. Chem. Soc.*, 1906, xxii., 24.)—The apparatus described obviated the use of numerous corks and rubber joints, and may be easily constructed in the laboratory.

The flask A, which may frequently be replaced by a wide test-tube, is filled almost to the neck with the liquid to be extracted, one-eighth to one-fifth of this volume of solvent being placed in the flask B, which is suitably heated. The vapour passes up the tube C, is condensed, and falling back, collects in the inner tube D, forming a column of liquid which in time becomes long enough to force its way through the liquid in A, and small drops of solvent, ascending in A, collect on the surface of the liquid, and finally overflowing at F, return to the flask B. On completion of the extraction, the solvent is run off from the neck of the flask by opening the stop-cock E.

W. H. S.
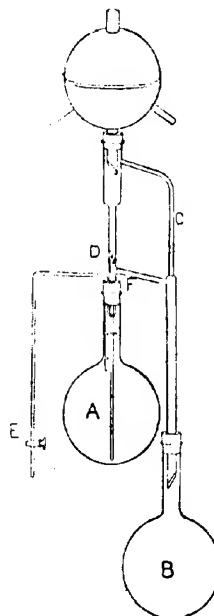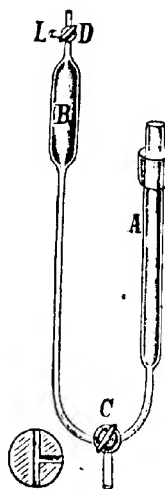
Apparatus for Removing Gases from Aerated Liquids before Determining the Specific Gravity of the Latter. K. Ulrich. (*Chem. Zeit.*, 1906, xxx., 90.)—The liquid is filled into the cylinder A and drawn into the bulb B by attaching the pipe L to an air-pump, the taps C and D being turned to give the necessary connections. The tap C is then closed, and the action of the pump allowed to proceed until the gases have been completely removed from the liquid in B. Air is now admitted by turning the tap D, and the liquid allowed to flow back again through the tap C into the cylinder A, where its specific gravity is taken by means of a hydrometer. The short tube below the tap C serves for emptying the apparatus.

W. P. S.

Note on a Combined Wash-Bottle and Pipette. J. W. Hogarth. (*Chem. News*, 1906, vol. 93, p. 71.)—By inserting the apparatus shown in an ordinary wash-bottle flask, a measured volume of solution may be delivered from the jet of the wash-bottle. The measuring vessel a, which is fitted with a jet and the mouth-piece f, is filled by raising the rod d, which closes the lower orifice, d', of a, and by blowing into the wash-bottle flask through the rubber-tube k. As soon as a is filled to the desired extent, the rod d is released, when the rubber-tube e, which connects d and the short piece of glass-tubing in the stopper through which it passes, forces the rod back into position, so as to close the lower opening of a. The vessel a is capable of holding 15 c.c., and of delivering any less quantity with an error of only $\frac{1}{3}$ c.c.
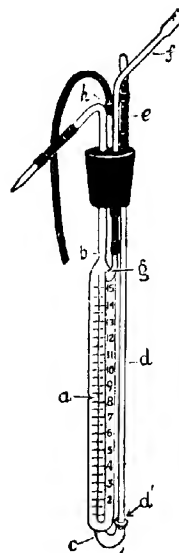
A. G. L.

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THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE monthly meeting of the Society was held on Wednesday evening, May 2, in the Chemical Society's Rooms, Burlington House. The President, Mr. E. J. Bevan, occupied the chair.

The minutes of the previous meeting were read and confirmed.

Certificates of proposal for election to membership in favour of Messrs. H. G. Harrison, M.A., E. Milier, and F. W. Passmore, Ph.D., were read for the second time; and certificates in favour of Messrs. William Dickson, Branksome, Bridge of Weir, N.B., analytical chemist, and Gordon Wickham Monier-Williams, B.A. (Oxon), Ph.D. (Freiburg). The Lammas, Esher, Surrey, analytical chemist, were read for the first time.

Messrs. F. W. M. Ross and F. E. Thompson were elected members of the Society.

The PRESIDENT announced that the Anniversary Dinner of the Society would take place at the Trocadero Restaurant on Wednesday, June 13, and that, for the convenience of country members, the monthly meeting would be held on the following evening -namely, Thursday, June 14.

The following papers were read: "The Estimation of Fat in Homogenized Milk," by H. Droop Richmond; "Milk Analysis," by H. Droop Richmond and E. H. Miller; "Note on the Composition of Saffron," by Albert E. Parkes; "On the Polenske Method for the Detection of Cocoanut Oil in Butter," by S. Rideal, D.Sc., and H. G. Harrison, M.A.; and "On the Presence and Detection of Cyanogen in Java and other Beans," by R. R. Tatlock and R. T. Thomson.

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THE DETECTION OF COCOANUT OIL IN BUTTER.

BY ARTHUR W. THORP.

(Read at the Meeting, March 7, 1906.)

THE addition of cocoanut stearin to butter has been an increasing practice since an odourless neutral fat was put on the market about 1897. From this date the number of samples examined showing an excessive amount of insoluble volatile fatty acids has gradually increased.

I have felt the need of a method of estimation of the insoluble acids which would be supplementary to the Reichert-Wollny determination, and I venture to think that a description of the method I have found to work satisfactorily in a commercial laboratory may be of interest.

The methods of Polenske (ANALYST, 1904, p. 154) and of Muntz and Coudon

(ANALYST, 1905, p. 155) involve the use of special distillation apparatus, and have not the advantage of the method I have practised. I determine the Reichert-Wollny figure, and then proceed to an approximate estimation of the insoluble volatile acids if the indications are suspicious.

I proceed as in the Reichert-Wollny test, but prefer heating the flask over a sand-bath instead of a naked flame. I distil off 110 c.c., and place the receiver in cold water for a short time. If there is any considerable quantity of cocoanut oil in the sample, oily drops will appear on the top of the distillate. I filter and titrate in the usual way, add 110 c.c. water to the flask, and distil off another 110 c.c. as before. I cool the second distillate, pour it over the same filter, and titrate the second filtrate; wash the apparatus with 50 c.c. alcohol and pour this over the filter, then wash the filter with another 50 c.c. of alcohol (90 per cent.), slightly warmed so as to hasten solution of the insoluble volatile acids; finally titrate the alcoholic solution with $\frac{N}{10}$ caustic soda and phenolphthalein.

The accompanying table of English butters blended by myself with cocoanut oil in varying proportions shows the result of my experiments. I also add the result of experiments with various foreign butters of undoubted purity and known origin.

It will be seen that the number of c.c. $\frac{N}{10}$ NaOH for pure butter was in no case higher than 8·4, whereas cocoanut oil requires 34 c.c.

	Reichert-Wollny Figure.	No. of c.c. $\frac{N}{10}$ NaOH registered by Second Filtrate.	No. of c.c. $\frac{N}{10}$ NaOH registered by Alcoholic Solution.
Butter fat	29·2	3·1	7·6
Cocoanut oil	8·0	4·0	34·0
Mixtures :			
90 per cent. butter fat, 10 per cent. cocoanut oil	27·1	3·7	10·2
80 ,, ,, 20 ,, ,,	24·6	4·0	15·5
70 ,, ,, 30 ,, ,,	23·4	4·0	18·1
60 ,, ,, 40 ,, ,,	21·5	3·9	20·1
50 ,, ,, 50 ,, ,,	19·4	4·2	21·8
40 ,, ,, 60 ,, ,,	17·6	4·4	24·4
30 ,, ,, 70 ,, ,,	15·1	4·2	26·0
20 ,, ,, 80 ,, ,,	13·3	4·4	27·1
10 ,, ,, 90 ,, ,,	10·6	4·4	29·1
Margarine	2·9	1·2	7·5
Italian butter	32·6	3·2	8·1
French butter	{ 31·1	3·6	7·4
	} 32·0	4·6	6·5
Australian butter	32·3	4·0	7·2
New Zealand butter	34·1	3·0	6·6
Argentine butter	31·0	3·1	6·2
Irish butter	27·8	2·9	5·2
Danish butter	33·4	3·7	7·1
U.S.A. butter	29·0	3·1	8·4
Russian butter	26·1	3·0	7·3

DISCUSSION.

The PRESIDENT (Mr. Bevan) said that he had had a sample which showed a Reichert-Wollny figure of 31 and a figure of something over 3 for the insoluble volatile acids, but in which the globules were perfectly oily at 10° C., and he had felt quite satisfied at the time that there was some cocoanut oil present, though the Reichert-Wollny figure of 31 did not leave room for much. Mr. Hehner, however, had since told him of a case in which a sample giving exactly similar results was proved beyond doubt to be genuine butter, so that the oiliness of the insoluble volatile acids at 10° C. seemed, after all, to mean nothing. To his mind the most promising test seemed to be the amount of soda absorbed by a certain proportion of the insoluble non-volatile acids. In the case of cocoanut oil the insoluble non-volatile acids from 1 gramme required 4·7 c.c. of normal soda solution, whereas in the case of genuine butter the figure varied from 3·8 to 3·85 c.c.

Mr. BODMER said that he had met with a case in which the insoluble volatile acids, which had a titration value of about 3·1 c.c. of decinormal soda solution, remained quite fluid even at 10° C. The Reichert-Wollny figure, however, was 30·3, which seemed to leave no room for any cocoanut oil. He had been trying to make the process of Knud Jensen and Kirschner, published recently in the ANALYST xxx. [1905], 205, 396) applicable to butter; but, although it worked very well with margarine, where the quantity of cocoanut oil was relatively large and the Reichert-Wollny figure low, in butter the smallness of the quantity of cocoanut oil present and the variations in the Reichert-Wollny figure for genuine butter threw out the formula altogether.

Dr. DYER said that the silver test mentioned by Mr. Bodmer had been tried in his laboratory for some time, and at first seemed likely to be useful; but on further experience it was found to break down. Some samples of butter believed to be pure gave quite distinct precipitates with silver nitrate.

Mr. F. J. LLOYD said he had found that in the spring pure butter fat sometimes contained relatively large quantities of liquid fats which were not present at other times of the year. In the case of one farm some years ago, with which he had to do, the fat was of so liquid a nature that when the milk was made into cheese the fat was actually squeezed out, and could not be retained by the curd.

Dr. RIDEAL said that he had made comparisons of the butter from different English counties, and had found considerable variation according to season and feeding. In some cases the figure for the insoluble volatile acids was more than 6 per cent. of the Reichert-Wollny figure, but as a rule English butters have a smaller ratio than found on the Continent by Polenske.

✛ ✛ ✛ ✛ ✛

THE COMPOSITION OF MILK.

By H. Droop Richmond, F.I.C.

(Read at the Meeting, March 7, 1906.)

Average Composition during 1905.—Of the 35,851 samples analysed in the Aylesbury Dairy Company's laboratory during 1905, 31,120 samples consisted of milk. The average composition of 14,828 samples of milk received from the farms is given in the table below :

Average Composition of Milk during 1905.

1905. Month.		Morning Milk.				Evening Milk.				Average.			
	Specific Gravity.	Total Solids.	Fat.	Solids-not-Fat.	Specific Gravity.	Total Solids.	Fat.	Solids-not-Fat.	Specific Gravity.	Total Solids.	Fat.	Solids-not-Fat.
January	...	1·0328	12·72	3·64	9·08	1·0325	13·09	4·02	9·07	1·0327	12·90	3·83	9·07
February	...	1·0329	12·63	3·56	9·07	1·0324	13·00	3·96	9·04	1·0327	12·81	3·76	9·05
March	...	1·0327	12·53	3·50	9·03	1·0324	12·89	3·90	8·99	1·0326	12·71	3·70	9·01
April	...	1·0326	12·41	3·43	8·98	1·0323	12·72	3·75	8·97	1·0325	12·57	3·59	8·98
May	...	1·0329	12·33	3·31	9·02	1·0324	12·76	3·77	8·99	1·0326	12·55	3·54	9·01
June	...	1·0327	12·22	3·27	8·95	1·0322	12·62	3·70	8·92	1·0324	12·42	3·49	8·96
July	...	1·0321	12·29	3·44	8·85	1·0315	12·52	3·76	8·76	1·0318	12·41	3·60	8·82
August	...	1·0318	12·30	3·51	8·79	1·0314	12·69	3·93	8·76	1·0316	12·50	3·72	8·74
September	...	1·0322	12·55	3·63	8·92	1·0319	12·92	4·02	8·90	1·0320	12·74	3·83	8·91
October	...	1·0327	12·72	3·68	9·04	1·0323	13·01	4·01	9·00	1·0325	12·86	3·84	9·02
November	...	1·0326	12·89	3·83	9·06	1·0322	13·16	4·15	9·01	1·0324	13·03	3·99	9·03
December	...	1·0325	12·72	3·73	8·99	1·0323	12·96	3·97	8·99	1·0324	12·81	3·85	8·99
Average	...	1·0325	12·53	3·51	8·99	1·0321	12·86	3·91	8·95	1·0323	12·70	3·73	8·97

The mean composition is practically the same as that found in 1904, the average percentage of fat differing only by 0·01 per cent. As usual, May and June are the lowest months for fat, and the winter months are the highest, while the usual drop in solids-not-fat was found in July and August. The difference between morning and evening milk, 0·37 per cent., agrees with that previously found.

Human Milk.—A sample of human milk was examined ; the composition was.

Total solids	...	...	...	...	...	13·97 per cent.	
Fat	...	..	...	...	...	..	5·61 ,,
Sugar	...	...	...	...	...	...	6·98 ..
Proteids	...	...	...	...	...	1·27 ,,
Ash	...	...	...	...	..	...	0·18 ,,
Solids-not-fat	...	...	...	...	...	8·36 ,,

Zeiss refractometer figure of the fat, at 35° C., 51·3°.

The fat globules were extremely large, ranging from 0·035 mm. in diameter to 0·002 mm., and the cream rose very rapidly.

Ass's Milk.—A sample of ass's milk was analysed by Mr. J. A. Goodson. It

was sour when received, but had not curdled, and was still in a state which allowed the analysis to be performed. His figures were :

Specific gravity	..	..	...		1·0362	
Total solids	...	...	...	.	10·27 per cent.	
Fat	...	...	...	.	...	...	1·45	,,
Sugar	...	...	...	...	...	...	5·65	,,
Proteids	...	..		...	...	2·09	,.
Ash	...	...	...	...	...	...	0·51	..
Solids-not-fat	...	...	...	..	8·82	.,
Acidity as lactic acid	...	..	...	...	0·51	.,

This milk is slightly above the average in fat, proteids, and ash.

Adulterated Cream.—Among the newer forms of adulteration of cream, the mixing of foreign fat and of condensed milk may be mentioned.

A sample of the former kind of cream contained :

Total solids	..	...	...	...	.	35·55 per cent.
Fat	...	...	..	..	...	28·95	.,
Sugar	...	..	...	...	...	3·28	.,
Proteids	.	...	...	...	.	2·36	,.
Ash	...	..	...	...	...	...	0·58	.,
Solids-not-fat	...	...	...	...	...	6·60	,,

The fat yielded the following figures :

Reichert-Wollny figure	...	.	...	21·5 and 21·8 c.c.
Potash absorption	...	...	...	...	21·63 per cent.

A cream adulterated with condensed milk had the following composition :

Total solids	...	...	...	...	...	48·51 per cent.
Fat	...	...	...	...	...	38·25	,,
Ash	...	...	...	...	...	.	0·76	.,
Solids-not-fat	...	...	...	...	.	10·26	.,

A recently-introduced Adulterant for Butter.—Butter is now adulterated with casein. A sample of the preparation used was examined. This sample was not exactly in the form in which it is added to butter, as the exact quantity of sodium carbonate necessary for neutralization and a considerable amount of salt are added before it is worked in. The composition was :

Water	...	...	.	...	...	..	65·47 per cent.
Fat	..	...	..	...	...	...	0·08	,,
Sugar	...	...	...	..	...	...	2·24	,,
Soluble proteids	...	...	..	...	0·69	,,
Ash of soluble portion	...	...	...	0·35	,,
Ash of insoluble portion	...	...	...	0·67	,,
Casein (by difference)	...	...	...	30·50	,,

From the large amount of chlorides present, this appears to be a badly-washed casein which has been precipitated by hydrochloric acid fr : separated milk.

To see the change of composition of butter, 5 per ce . of this was worked into

some butter. The salt, which was added to the genuine butter, was omitted in the portion to which the casein was added. The composition of the two samples was:

					Genuine Butter.		Butter plus Casein.
Water	...	...	...	...	13·51	...	16·02
Fat	...	...	...	...	83·92	...	82·08
Curd ...	...	...	...	...	0·96	..	1·90
Casein	...	...	...	...	0·23	...	1·08
Salt	...	...	...	...	1·61	...	None

The casein was determined by extracting the "curd" with dilute ammonia, filtering, and precipitating with dilute acetic acid. I have found the average amount of casein in genuine butters (unwashed) to be 0·38 per cent., and not to exceed 0·50 per cent.

A New Preservative.—A sample of preservative which came into my hands proved to be acid potassium fluoride (KHF_2); it is in the form of semi-transparent flat crystals, very little hygroscopic, and very soluble in water. I found:

Potassium	...	49·7	per cent., calculated	50·1	per cent.
Acidity as HF	...	24·9	,,	,,	25·5	,,
Loss on ignition	...	25·45	,,	,,	25·5	,,

DISCUSSION.

The PRESIDENT (Mr. Bevan) said that he was afraid that the adulteration of butter with casein was only too common. He had lately met with several samples containing 4 to 5 per cent. of curd, always accompanied by a large proportion of water. Milk-sugar also was generally present, pointing to the addition of condensed milk.

Mr. BLOUNT said that he should be interested to hear whether the use of potassium hydrogen fluoride was at all common, because some fifteen years ago when fluorides were suggested as a preservative for fish, he had himself for the purpose of experiment taken a small quantity of sodium fluoride, and had in consequence suffered from acute indigestion.

Mr. RICHMOND said that he did not know that potassium hydrogen fluoride was much used. It came into his hands in rather a roundabout way from the United States. It was said to be perfectly harmless and to preserve all kinds of food, and was put on the market under the name of "acid potassium oxalate!"

Mr. L. MYDDELTON NASH asked in what way the extra casein was worked into the butter; whether it was churned in in a freshly precipitated condition, or was first dissolved in a trace of alkali. He had lately received a formula from America, one of the constituents of which was "potassium oxalate." He had been at a loss to understand the reason for including such an ingredient, but Mr. Richmond's statement that potassium fluoride was sold as such somewhat enlightened him.

Mr. A. E. PARKES said that in 622 samples of milk which he had examined during the past year under the Sale of Food and Drugs Acts, the average proportion of fat was 3·52 per cent., even including 21 per cent. that were adulterated, showing how low the standard for fat adopted by the Board of Agriculture is.

Mr. F. J. LLOYD thought that erroneous ideas were likely to be derived from the averages of such very large numbers of samples as were dealt with in this paper. In his experience the milk produced during June had never been so poor in fat as it was in 1905. At the Bath and West of England Society's Show in particular a much larger percentage of the cows than usual were disqualified for the milking trials because their milk was below the required standard of 3 per cent. With regard to cream, he had been informed privately that a large quantity containing foreign fat was now being put on the market. He had recently found fluorides in both butter and cream.

Mr. J. F. LIVERSEEGE said that he had lately met with cream containing starch. It was not very easy to estimate the proportion. He had found the simplest way to be to determine the total solids, fat, milk-sugar, ash, and nitrogen, and to take the starch by difference. The average percentage of fat in the samples of milk bought under the Act in Birmingham in 1905 was 3·6. He should like to ask Mr. Richmond how far the cows represented by his figures were stripped; and he should also be interested to hear Mr. Richmond's opinion as to the effect of different modes of feeding on the quality of the milk.

Dr. VOELCKER said that it was certainly the case that both at the Bath and West of England and at the Royal Agricultural Society's Shows in 1905 there was a larger number than usual of morning milk samples showing low results; but he was far from thinking that such samples were really to be taken as fair guides. Considering all the circumstances attending the exhibition of animals away from their own homes, and amid the disturbing surroundings of agricultural shows, it was only a very well-trained animal that would be likely to give good results. Indeed, he would go so far as to say that what show animals were required to do was something abnormal — namely, to produce a larger quantity of milk than they would produce under normal conditions, the prizes, rightly or wrongly, being generally given for the largest quantity of milk, provided that it reached a certain standard of quality. He thought that conclusions drawn from the results of such show-yard tests had little bearing on the quality of the average milk supplied by the farming industry of this country to the public.

Mr. M. WYNTER BLYTH thought that Mr. Richmond's figures could not be considered to represent quite normal milk, because the farms were specially selected, and the farmers, knowing that the milk would be analysed, would take care to keep up to a certain standard. At Brighton samples of milk were regularly taken at railway-stations as they came direct from the farmers, and last year the proportion of these falling below the standard had been greater than ever before. That might be attributed either to a bad year, or to efforts on the part of the farmers to " break down " the milk to the standard of 3·0 per cent., as laid down by the Sale of Milk Regulations. He thought that the Regulations had had a bad rather than a good effect, and he considered that it would be better to have a fixed standard, and to allow no excuse whatever for departing from it. Mr. Richmond's figures seemed to support that view, for although in his (the speaker's) opinion they could not be regarded as normal for the whole country, they showed what could be done on a well-managed farm.

Mr. Richmond said that the casein was precipitated from skim milk with acid and pressed fairly dry; sufficient sodium carbonate was added to neutralize the acid exactly, and the casein was then worked into the butter. There were, practically speaking, no samples low in solids-not-fat, and it was only in May and June that any extensive numbers of samples low in fat were observed. There also were a few samples low in fat in April and July, but in the other months of the year they were rare. It was only the morning milk which need be considered, as even in May and June the fat in the evening milk hardly ever fell below 3·0 per cent. The table below gives the percentage of samples of *morning milk* falling below 3·0 per cent. of fat during May and June for each year since 1900 :

MORNING MILK ONLY.

Month.		Fat 2·9 to 3·0.		Fat 2·8 to 2·9.		Fat 2·7 to 2·8.		Fat below 2·7.
May, 1900	... ...	4·1	...	0·9	...	0·4	...	—
June, 1900	... ...	3·0	...	2·0	..	0·4	...	0·2
May, 1901	... ...	4·0	...	2·0	...	1·6	...	0·4
June, 1901	... ...	2·0	...	1·4	...	—	...	0·4
May, 1902	... ...	2·2	...	2·0	...	0·8	...	· ·
June, 1902	... ...	1·7	...	1·5	...	0·4	...	····
May, 1903	.. ...	2·0	...	0·9	...	—	...	—
June, 1903	... ...	1·7	...	0·6	...	0·8	...	—
May, 1904	... ...	2·7	...	1·8	...	0·9	...	0·5
June, 1904	... ...	3·6	...	3·2	...	0·8	...	0·2
May, 1905	... ...	6·0	...	2·0	...	0·6	...	0·2
June, 1905	... ...	3·1	...	2·0	...	0·2	...	· ·

His experience was that, practically speaking, 1905 was no worse a year for milk than any other of the last five years. A little variation occurred from year to year, sometimes in the one direction, sometimes in the other; but although the milk of 1905 was a little less rich than that of 1903, which was one of the best years, it was better than that of 1900, and about equal to that of the other years. He did not know of any very good method for the estimation of starch in cream. Probably that adopted by Mr. Liverseege would give fairly good approximate results. He thought that in most cases the cows would be thoroughly stripped, because the milk had to be supplied to a certain standard. He was afraid that the shortness of the time remaining would not allow of his going into the question of the effect of feeding. He thought the figures he had given were fairly representative of normal milk, although the farms were to some extent selected, because the selection had no reference to the composition of the milk, but to the water-supply and sanitation, and in his experience the farmers did not take any special steps to obtain milk of more than average quality because they knew that the milk was regularly analysed, as each farmer believed that his milk was richer than anyone else's.

Dr. Schidrowitz suggested that the starch might be estimated simply by extracting the cream with water, taking out the fat with ether, treating the residue with a solution of malt extract after gelatinizing, filtering off, and determining the optical rotation and copper-reducing power.

THE DETERMINATION OF HIGHER ALCOHOLS IN SPIRITS.—II.

By PHILIP SCHIDROWITZ, Ph.D., and FREDERICK KAYE, A.R.C.Sc.

In our first paper on this subject (ANALYST, June, 1905) we gave the details of our revision experiments on the Beckmann process, and also some few facts concerning the Allen-Marquardt process. In the present communication we wish to record a series of experiments on the Allen-Marquardt process and on the colorimetric (sulphuric acid) method.

B. The Allen-Marquardt Process.

The purification of materials and the apparatus employed were described in our previous paper, and need not, therefore, be referred to again here.

The first series of figures (Table 1.) relates to the oxidation of amylic alcohol dissolved in carbon-tetrachloride with chromic acid mixture- that is to say, the quantities of the higher alcohol stated to be present were added directly to the carbon-tetrachloride, and were not obtained by extraction from a dilute alcoholic solution of brine. The object was to ascertain the behaviour of amylic alcohol as such in varying proportions and conditions of the process of oxidation.

TABLE I.

Oxidation of Amylic Alcohol in Carbon-tetrachloride Solution.

(Carbon-tetrachloride 100 c.c. ; oxidation mixture, 5 grams bichromate of potash, 30 c.c. H_2O, 1·5 c.c. strong H_2SO_4.)

No. of Experiment.	Weight of Amylic Alcohol present (Grams).	Weight of Amylic Alcohol found (Grams).	Percentage Gain or Loss.	Duration of Oxidation (Hours).	Remarks.
1	0·0990	0·0952	− 3·8	8	
2	0·1000	0·0942	− 5·8	8	
3	0·1066	0·0982	− 6·0	8	
4	0·1178	0·1007	− 14·5	8	Double quantity of oxidation mixture.
5	0·1640	0·1610	− 1·8	8	
6	0·1740	0·1760	+ 1·1	8	
7	0·1770	0·1810	+ 2·0	8	
8	0·1874	0·1582	− 15·5	8	
9	0·2367	0·2112	− 15·0	8	
10	0·3324	0·2877	− 13·4	8	Double quantity of oxidation mixture.
11	0·1864	0·1703	− 8·0	10	
12	0·1970	0·2020	+ 7·0	10	
13	0·4140	0·3362	− 18·7	8	
14	1·5338	1·1325	26·1	8	Triple quantity of oxidation mixture.

From the above table the following conclusions may be drawn: When the quantity of higher alcohol is not in excess of that ordinarily found by the process in commercial spirits—*i.e.*, up to 0·15 per cent.—the results are very accurate as far as the oxidation is concerned, with a boiling period of eight hours. When the quantity of higher alcohol is substantially above 0·15 per cent., a boiling of ten hours appears desirable (*cf.* Nos. 11 and 12 with Nos. 8, 9, and 10). When the quantity of higher alcohol is markedly over 0·3 per cent. (Nos. 13 and 14) a variation of the method is obviously necessary. This is of little practical importance, as commercial spirits such as whisky and brandy rarely contain more than 0·13 per cent.

Table II. gives the results obtained by adding known quantities of amylic alcohol to 100 c.c. of pure 50 per cent. ethylic alcohol, diluting with brine and extracting with CCl_4 in the usual manner, and then oxidizing as above.

TABLE II.

Results of the Allen-Marquardt Process obtained by Working with 50 per cent. Solutions of Ethylic Alcohol containing known Amounts of Amylic Alcohol.

No. of Experiment.	Weight of Amylic Alcohol taken (Grams).	Weight of Amylic Alcohol found (Grams).	Percentage Gain or Loss.	Duration of Oxidation (Hours).
15	0·0610	0·0616	+ 1·0	9
16	0·0942	0·0915	− 2·8	8
17	0·1004	0·1056	+ 5·0	9
18	0·1407	0·1390	− 1·2	8
19	0·1472	0·1415	− 3·9	10
20	0·1992	0·1624	− 18·4	8
21	0·1992	0·1654	− 17·1	8
22	0·2008	0·1693	− 15·6	8
23	0·2008	0·1725	− 14·0	8
24	0·2060	0·2187	+ 6·0	10
25	0·2077	0·2128	+ 2·4	10
26	0·3776	0·3243	− 14·0	10
27	0·3450	0·3432 ·	− 0·5	12

The above results plainly indicate that the process as a whole gives very accurate results when the quantity of higher alcohol is not greater than, roughly, 0·15 per cent. (Nos. 15 to 19). When the percentage of higher alcohol substantially exceeds 0·15 per cent., but does not rise materially above 0·2 per cent., it is necessary to prolong the period of boiling somewhat (*cf.* Nos. 20 to 23 with Nos. 24 and 25). It is obvious, however, that quantities up to 0·35 per cent. can readily be dealt with if the duration of oxidation is extended to twelve hours. In view of the fact, to which we have alluded above, that commercial spirits rarely exceed 0·15 per cent., and that it has now been amply demonstrated that this amount can be successfully dealt with in eight hours with brisk boiling, we do not advocate extending the time to ten or twelve hours, but would suggest that if a result showing more than 0·14 per cent.

be obtained, the analysis should be repeated after diluting the spirit with a convenient quantity of pure 50 per cent. alcohol, or taking a smaller quantity of the sample.

We may add that we have examined several hundred samples of commercial spirits (whisky* more particularly) by this method, and only in the rarest cases have we obtained figures which might be regarded as doubtful. With a little practice the process works smoothly, and the abnormal results which may cause trouble to the novice will be found to become very exceptional indeed. When it is considered that the oxidation is carried out in an open vessel —*i.e.*, not under pressure in a sealed flask or tube—we think it will be admitted that the accuracy of the results obtainable is remarkable. We have little doubt that if the oxidation were performed in a pressure bottle the results might be still more satisfactory, and we intend to make some experiments in this direction in the future. We propose also to make some further experiments in which butylic and propylic alcohols will be substituted for amylic alcohol.

Before leaving the Allen-Marquardt process, it is necessary to refer to some observations and experiments we have made concerning the estimation and nature of the "mineral acid." Allen (ANALYST, 1891) states that the "mineral acid" formed in the course of the process corresponds to, roughly, 2 c.c. of decinormal baryta, and that the actual amount may be estimated by titrating in the first place with baryta, using methyl orange as indicator, and afterwards adding phenolphthalein in order to estimate the organic acids. In the course of a very large number of estimations we noticed that the amount of "mineral acid" thus determined varied widely, but that, almost without exception, it amounted (expressed in terms of the number of c.c. of decinormal baryta employed) to, roughly, one-tenth of the whole. In view of the singularity of this fact, we thought it desirable to make some estimations of chlorine in the solutions finally obtained, in order to ascertain whether this corresponds to the amount of "mineral acid" found by titration. The following figures were obtained:

TABLE III.

No. of Experiment.	Chlorine found (Grams).	Chlorine calculated (Grams).
1	0·0023	0·0070
2	0·0012	0·0085
3	0·0012	0·0108
4	0·0039	0·0136
5	0·0014	0·0094
6	0·0007	0·0107
7	0·0006	0·0139
8	0·0014	0·0065

It will be observed that in every instance the amount found was very much smaller than the calculated quantity. Indeed, whereas the amount calculated

* *Cf.* Schidrowitz and Kaye, "The Chemistry of Whisky"—II., *Journ. Soc. Chem. Ind.,* June, 1905.

generally approaches to or exceeds a centigram, the amount found is so small in most cases as to be within the experimental error.

It is obvious that the only mineral acid which might reasonably be supposed to be present is hydrochloric acid. These results led us to think that the so-called "mineral acid" might not be mineral acid at all, but that its apparent presence might simply be due to the fact that some organic acids are not without effect on methyl orange. It has long been known (*cf.* Glaser, "Indikatoren der Acidimetrie u. Alkalimetrie," p. 23 *et seq.*, and Schidrowitz, ANALYST, August, 1903) that acetic acid in aqueous solution reacts with methyl orange, and, on the other hand, that this reaction may be prevented, or the pink reaction colour caused to disappear by the addition of a sufficiency of a non-electrolyte such as alcohol or acetone, but we are not aware that the action of aliphatic acids on the indicator has been the subject of quantitative examination. If the explanation of the nature of the "mineral acid" which suggested itself to us were correct, it would follow : (1) That the addition of alcohol or acetone to the ultimate distillates obtained in the Allen-Marquardt process would prevent the appearance of, or, if added subsequently to the addition of the indicator, cause the disappearance of the pink coloration reputedly due to "mineral acid"; and (2) that aliphatic acids such as butyric and valeric acids would in conditions of solution approximating to those of the Allen-Marquardt process show similar results.

Ad. 1.—On examining a number of ultimate distillates of the Allen-Marquardt process on the lines indicated it was found that when an equal volume of alcohol or acetone was added to the solution prior to the addition of the indicator the colour obtained was a pure yellow, and similarly, that when the alcohol or acetone was added to the solution after the indicator had been run in, the solution, which had been a distinct pink, reverted to a plain yellow. In these same test cases also it was found (by titrating an aliquot part of the solution) that the apparent "mineral acid" was quite normal—*i.e.*, about one-tenth of the whole.

Ad. 2. — Some preliminary experiments have been made with acetic, butyric, iso-butyric, and valeric acids, and these entirely confirm the hypothesis stated above. The following figures were obtained :

TABLE IV.

Acetic Acid.

No. of Experiment.	Volume of Solution.	Acetic Acid calculated (Grams in Solution).	Acetic Acid found (Grams in Solution).	C.C. $\frac{N}{10}$ Baryta, using Methyl Orange (=apparent Mineral Acid).	C.C. $\frac{N}{10}$ Baryta, Total for Methyl-orange and Phenolphthalein Titrations.	Ratio of Total Titration to Methyl-orange Titration.
1	100 c.c.	0·1334	0·1331	3·35	22·18	6·5 : 1
2	,,	0·0667	0·0665	1·35	11·09	8·2 : 1
3	,,	0·0333	0·0332	0·68	5·54	8·2 : 1
4	,,	0·0333	0·0332	0·68	5·54	8·2 : 1
5	,,	0·0266	0·0276	0·54	4·60	8·5 : 1
6	,,	0·0200	0·0192	0·40	3·52	8·8 : 1
7	,,	0·0133	0·0146	0·27	2·44	9·0 : 1

Butyric Acid.

8	100 c.c.	0·1614	0·1654	2·21	18·80	8·4 : 1
9	,,	0·1077	0·1100	1·19	12·50	10·1 : 1
10	,,	0·0538	0·0544	0·54	6·19	11·4 : 1
11	,,	0·0215	0·0228	0·22	2·60	12·0 : 1

*Iso-butyric Acid.**

12	100 c.c.	0·0835	0·0882	1·61	10·02	6·1 : 1
13	200 c.c.	0·0835	0·0896	1·47	10·18	6·9 : 1
14	100 c.c.	0·0417	0·0448	0·73	5·09	6·9 : 1
15	200 c.c.	0·0417	0·0448	0·65	5·09	7·8 : 1
16	250 c.c.	0·0417	0·0448	0·39	5·09	10·0 : 1

Valeric Acid.

17	50 c.c.	0·0211	0·0209	0·33	2·05	6·2 : 1
18	100 c.c.	0·0422	0·0419	0·68	4·11	6·2 : 1
19	150 c.c.	0·0422	0·0419	0·57	4·11	7·2 : 1
20	200 c.c.	0·0422	0·0419	0·49	4·11	8·3 : 1
21	250 c.c.	0·0422	0·0426	0·49	4·18	8·5 : 1

From the above figures it would appear that there is some quantitative relationship between the total acid found by titration and the apparent "mineral acid" on the one hand and between the concentration of the solution and its total volume (as compared with the amount of indicator employed) on the other. The above experiments are of a preliminary nature only, and it would be premature, therefore, to discuss the action of methyl orange on aliphatic acids further at present. We intend to pursue this matter in the future, as it presents a wider interest than that which associates it with the present communication; but as far as the latter is concerned, it is quite clear that the result of the preliminary titration for "mineral acid" in the Allen-Marquardt process may be neglected when the figure obtained is less than or roughly equal to one-tenth of the whole. In doubtful cases, or where great accuracy is desired, a gravimetric estimation of chlorine is indicated.

C. The Colorimetric (Sulphuric Acid) Process.

This process, as is now fairly well known in this country (*cf.* Girard et Cuniasse, "Manuel pratique de l'Analyse des Alcools et des Spiritueux"; Paris, Masson, 1899) is based upon the fact that certain higher alcohols, when heated with strong sulphuric acid, give rise to a more or less marked coloration, the intensity of the coloration observed being taken as a measure of the quantity of the higher alcohols present. Numerical expression is given to the colour intensity by comparing the liquid under examination with a standard control solution or solutions, iso-butyric alcohol being the standard higher alcohol generally employed for this purpose. We have repeatedly (ANALYST, June, 1905 ; *Journal of the Society of Chemical Industry*, June, 1905, etc.) pointed out the cardinal defects which such a process must possess.

* It is obvious that the iso-butyric acid employed was not quite pure.

In view of the fact that others besides ourselves (Girard et Cuniasse, *loc. cit.*, Mohler, *loc. cit.*; Vasey, "The Analysis of Potable Spirits"; Allen, *Journal of Federated Institute of Brewing*, 1897; Veley, *Journ. Soc. Chem. Ind.*, May 15, 1906, etc., and numerous private communications to the authors) have published facts and figures demonstrating the defects of *principle* inherent in the sulphuric acid process, we cannot but express surprise at the assurance with which results based on this process are put forward. The defects of the process may be summarized under two headings : (1) Defects of Principle, and (2) Defects in Practice.

Defects of Principle.—The main objection to the process under this heading is contained in the fact that the coloration produced by various higher alcohols differ enormously. Thus, if the coloration due to iso-butyric alcohol be taken as $= 10$, then the colorations due to caprylic alcohol, œnanthic alcohol, amylic alcohol, and the propylic alcohols are 11, 7, 3, and 0 respectively (Mohler, *loc. cit.*). More recently Veley (*loc. cit.*) has published some experiments which throw doubt even on the comparative accuracy of these figures, and it appears probable that the colorations produced are really not due to the higher alcohols at all, but to the traces of impurities they contain. If this is so, it goes far towards explaining the widely different results obtained by different chemists when working on identical samples. However that may be, it must be remembered that the higher alcohols in any given commercial spirit are mixtures, and there is little doubt, in view of the work of Bell, Rabuteau, Ordonneau, and others, that the proportions of the various higher alcohols in any given *type* of spirit (*i.e.*, whether pot still or patent still whisky, or brandy, etc.) differ according to the type. Moreover, in view of recent work on the formation of the higher alcohols in fermenting worts (Ehrlich), it is plain that even in the same type of spirit the composition of the "fusel" will vary considerably.

In consideration of all these facts, the argument that if a particular alcohol be chosen as the standard or "type," that all results obtained will be of a strictly comparative nature, seems to us to be absolutely untenable ; for, in order that this should be the case, it would have to follow that the proportions of the various higher alcohols to one another in any given spirit would have to be a constant, and that the higher alcohol used for the control should be of the same degree of purity (or rather impurity) at all times. There is, however, another grave objection of principle to this process, and that is that there are undoubtedly other substances in spirits besides higher alcohols and besides those which are purposely removed by means of potash or some other dealdehyding reagent), which give a coloration with sulphuric acid. We are unaware of the exact nature of these substances, of their quantity, and of the intensity of coloration they produce, and from our very numerous experiments we have reason to believe that the presence of these substances is of far greater practical importance than has hitherto been suspected (*cf.* our paper on this subject, ANALYST, June, 1905, and discussion thereon). It has been suggested that even if this process does not yield results referring to higher alcohols only, it is, nevertheless, a valuable comparative index of the nature of a spirit. To this we demur, mainly because of our lack of exact knowledge concerning the substances other than higher alcohols which do produce coloration.

and because our analytical experience (see tables below) has shown us that the coloration produced by these substances is out of all proportion to the actual higher alcohols, and that it is not even in the narrowest sense indicative of the nature of the spirit examined. It appears to us, therefore, in any case unwarrantable to place on the same numerical or quantitative basis figures referring, on the one hand, to substances of a definite chemical nature, such as the esters, acids, and aldehydes, and, on the other hand, to higher alcohols plus substances of unknown quantity or colorimetric effect. That is to say, assuming that the " colorimetric test " is an index figure of quality, it should be separately returned, and not included in the quantitative " coefficient of impurities."

Defects in Practice.—Of a very real nature is the difficulty of preparing specimens of " pure " iso-butylic (or amylic) alcohol of constant colorimetric intensity for purposes of the control or " type " solutions. If Veley's statements are accepted, this appears to be an absolutely insurmountable objection to the process. The remaining defects in practice (apart from those involving questions of principle) are mainly ascribable to the numerous modifications in detail practised by different workers. To begin with, no less than four different de-aldehyding reagents have been proposed. All of these are apparently in use, and it is unfortunately a fact that the results may differ very considerably, according to the reagent employed. The method of heating the alcoholic solution with the sulphuric acid, again, is of the greatest practical importance (see below), and yet no two workers appear to use exactly the same method. Finally, we are by no means sure that the same method of calculating the amount of " higher alcohols " from the observed coloration is employed by all chemists. We have come across results which have indicated to us that those responsible for the figures are under the apprehension that the coloration observed stands in direct ratio to the " higher alcohols." This, of course, is only the case when the liquid under examination and the control solution exhibit practically equal intensities. We now proceed to give some figures bearing on the points raised above.

1. *Figures illustrating Defects in Principle.*—In a recent number of the *Journal of the Society of Chemical Industry* (June, 1905) we published a series of analyses of whiskies in which the higher alcohols were determined by the Allen-Marquardt and the colorimetric (using an amyl alcohol control) methods respectively. The number of analyses was about one hundred. The results by the latter process are throughout much higher than those obtained by the former; but it would follow that if the composition of the "fusel" was substantially the same in all whiskies, and if the other substances producing coloration were negligible or present in quantities bearing some fixed ratio to the "fusel" (*i.e.*, higher alcohols), the ratio of the results obtained by the two processes would be practically a fixed quantity. This is, however, far from being the case, even for whiskies of the same class. The following table shows the maximum and minimum ratios observed in each individual class of whisky for results obtained by the two processes in individual samples of the spirit:

TABLE V.

Ratios of Figures obtained by the Allen-Marquardt and Colorimetric Processes respectively (Amylic Control).

Type of Whisky.	RATIO OF ALLEN-MARQUARDT TO COLORIMETRIC RESULT	
	Maximum Ratio.	Minimum Ratio.
Highland malt	1 : 6·1	1 : 2·0
Lowland ,, ...	1 : 5·5	1 : 1·9
Campbeltown	1 : 4·6	1 : 2·0
Islay	1 : 4·6	1 : 3·1
Grain (patent still) ...	1 : 6·6	1 : 0·8

It will be noticed that the variations in each class of whisky are very large Since the results on which the above figures are based were published we have made a considerable number of comparative experiments, in which both the iso-butylic and amylic controls were employed. We append a few of the results obtained herewith:

TABLE VI.

Parallel Determinations of " Higher Alcohols " by Three Methods.

No. of Experiment.	Type of Spirit.	Allen-Marquardt (Oxidation Method).	COLORIMETRIC METHODS.	
			Iso-butylic Control.	Amylic Control.
1	Patent still	300*	204*	1055*
2	,,	70	64	102
3	,,	58	120	370
4	,,	52	46	55
5	Pot still	145	156	628
6	,,	185	284	1160
7	,,	147	150	430
8	,,	217	208	320
9	,,	351	248	768
10	Blend	146	155	447
11	,,	193	212	431
12	,,	92	142	354
13	,,	76	76	107
14	,,	77	149	191
15	,,	43	115	131
16	,,	81	208	245
17	,,	47	181	334
18	,,	53	250	410

* The numbers refer to parts per 100.000 of absolute alcohol throughout.

The above results, which we have selected from a large number, are fairly representative. It will be noticed (1) that the results obtained with the iso-butylic control are generally much lower than those obtained with the amylic; (2) that in some cases the results by the oxidation and colorimetric (iso-butylic) methods approximate very closely, but that, on the other hand, they frequently diverge to a very marked extent; (3) that generally the results by the oxidation method are a good deal lower than those by the colorimetric (iso-butylic), but that this is by no means always the case; (4) that in some cases the results by all these processes are fairly close. It is obvious that the greatest divergence will occur in those cases in which the mean composition of the higher alcohols differs widely (as far as their colorimetric properties are concerned) from the alcohol used as a standard type, or when the proportion of substances other than higher alcohols, which react colorimetrically with sulphuric acid, is high. It should be noted that the above colorimetric results were obtained by heating in the water-bath for an hour with sulphuric acid, after the spirits had been de-aldehyded by means of Hewitt's reagent (phenylhydrazine p sulphonate of lime).

TABLE VII.

Figures illustrative of Defects in Practice.

(a) *Use of Different Dealdehoding Reagents.*

No. of Experiment.*	REAGENT USED.	
	Hewitt's Reagent.	Meta-phenylene-diamine hydrochloride
1	194	184
2	182	189
3	345	227
4	150	179
5	528	480

TABLE VIII.

(b) *Use of Different Methods of Heating. Control, Iso-butylic Alcohol).*

No. of Experiment.†	METHODS OF HEATING.	
	Naked Flame.	Water-Bath (one hour).
1	194	116
2	150	116
3	345	115
4	238	131
5	227	126

* The control used in the above series was iso-butylic alcohol. The heating was conducted over a naked flame.

† De-aldehyding reagent used in above series—Hewitt's reagent. All the above were whiskies.

In the following series are set out the results obtained by five different methods :

TABLE IX.

Process.

COLORIMETRIC (ISO-BUTYLIC CONTROL THROUGHOUT).

No. of Experiment.	Allen-Marquardt.	De-aldehyding Reagent.			
		Hewitt's Reagent.		M.-phenylene-diamine-hydrochloride.	
		Naked Flame.	Water-bath.	Naked Flame.	Water-bath.
1	103	194	116	184	97
2	87	150	116	179	140
3	69	160	138	154	139
4	112	345	145	227	185
5	85	238	131	244	169
6	78	258	177	274	84
7	92	227	126	191	172

All the above were whiskies.

It will be observed that the "water-bath" colorimetric results are closer to the oxidation figures than those obtained by heating over a naked flame.

De-aldehyding Reagents.—The only reagent which to our knowledge removes the aldehydes completely and without apparently bringing about any secondary reactions is phenyl-hydrazine-sulphonate of lime (Hewitt's reagent). Meta-phenylene-diamine-hydrochloride, which is strongly recommended by some French chemists, does not always remove the furfural completely from commercial spirits, as the following figures show :

TABLE X.

No. of Experiment.	Total Furfural.	Furfural not removed by M.-phenylene-diamine-hydrochloride.
1	2·9	0·75
2	2·8	0·78
3	3·0	0·92
4	2·5	0·46

These figures were obtained by working on whiskies. The quantity of the de-aldehyding salt employed was 1·5 grams for 50 c.c. of spirit. It appears that the failure of the reagent to remove furfural completely is due to a secondary reaction, for solutions of furfural in pure 50 per cent. alcohol,-containing far more furfural than the whiskies referred to, were completely defurfuralized by the reagent. The same result was obtained with solutions of furfural *plus* acetic aldehyde in pure

50 per cent. alcohol. Thus, a 50 per cent. ethylic alcohol solution to which 10 parts of furfural per 100,000 of absolute alcohol had been added was completely defurfuralized by means of 1·5 grams of the reagent ; and the same result was obtained with a solution containing 10 parts of furfural and 24·5 parts of acetic aldehyde. It is obvious that the non-removal of all the furfural in the case of commercial spirits is another source of error in the higher alcohol figures obtained by means of the diamino reagent, inasmuch as furfural, as is well known, acts as an intensifier to the action of the sulphuric acid. It is curious that, nevertheless, the results obtained with the reagent in question are generally lower than those recorded when Hewitt's reagent (which completely removes furfural and aldehydes) is used. We believe that this is due to the fact that the meta-phenylene-diamine reagent enters, in the case of commercial spirits, into secondary reactions with some of the less known " impurities." The facts recorded above indicate that this is so, but we have also noticed that a peculiar fluorescence is produced by this reagent, either in the spirit before distillation, or in the distillate, or in both. We have also observed the fact that in those cases in which furfural is incompletely removed the fluorescence is only marked in the spirit prior to distillation, and that the distillate is then colourless. On the other hand, when the phenomenon of fluorescence is slight in the liquid prior to distillation, but strongly developed in the distillate, the latter shows little or no furfural.

Regarding other de-aldehyding reagents, we have found phosphate of aniline useless, as its use invariably results in the presence of aniline in the distillate. We have made some experiments with caustic alkalies, but the number of experiments made is not sufficient to warrant our expressing any definite opinion. We can only say that if, after considering all the facts set out in this paper, some of our colleagues still desire to continue the use of a colorimetric higher alcohol process, they will be well advised in using Hewitt's salt as a de-aldehyding reagent. Our own conclusion regarding this matter is that there is only one process which is to any degree reliable, and that is the oxidation process. By modifying the conditions of working, the colorimetric process may be made to give almost any figure one pleases ; and indeed, in practice, we have found that results returned by different observers (both using an iso-butylic control) have differed by more than 100 per cent.

<div align="center">DISCUSSION.</div>

The PRESIDENT (Mr. Bevan) having invited discussion,

Dr. HEWITT said that he was pleased to hear that the authors intended to check the values obtained by the oxidation process in the case of butyl alcohol and propyl alcohol. To his mind this was a matter of absolute necessity, because, although by addition of brine to a specific gravity of 1·1 and extraction with carbon tetrachloride the whole of the amyl alcohol was certainly extracted, nevertheless there was no proof that the whole of the propyl alcohol that might be present would be extracted, since at ordinary temperatures propyl alcohol was miscible with water in all proportions, though probably at a lower temperature the mixture of propyl alcohol and water would separate out as amyl alcohol and water did at ordinary temperatures. With so great a difference in water solubility it seemed essential to know

exactly what happened. He was very glad to find that the methyl orange titration for " mineral acid " could be dispensed with, in the first place because he found it rather difficult at any time to get the end-point with this indicator, which was not a very handy one to use. He did not think that he was altogether peculiar in this respect. In the second place, in dealing, as in this case, with an acid that was only very incompletely ionized, the end-point must of necessity be very far from sharp. He had never worked out the ratio, but it had always struck him that the more higher alcohols he found in a spirit, the more mineral acid apparently came over. This, of course, was what, on thinking over the matter, one would expect. With regard to the colorimetric method, he had himself used it in a great many cases, and he thought that probably others had too. Of course there were two ways of looking at it. From a scientific point of view it must be agreed that the colorimetric method was useless ; but he did not feel quite sure that the possibility of its affording an index of quality had even now been entirely got rid of. The way in which errors arose was obvious from what the authors had said as to the cause of the coloration. The iso-butyl alcohol might be rectified, but with iso-amyl alcohol there was a difficulty, because in ordinary commercial iso-amyl alcohol there were the active alcohol boiling at just over 120° and the alcohol boiling at $131\frac{1}{4}°$. Which of these two gave the stronger coloration was not known, and it would be very difficult for two workers to get specimens exactly alike. He had recently made some experiments in this direction, and had found it possible, by repeated fractionation of samples bought as pure, to get the higher fraction with the correct boiling-point within about $\frac{1}{4}°$. Probably that was fairly pure iso-butyl carbinol. It was, however, very easy to get small admixtures, the effect of which was unknown. No doubt the authors had worked in every case with the same iso-amyl alcohol, and had carefully purified it ; but on looking at the results one found very varying ratios between the figures obtained with iso-butyl alcohol and with iso-amyl alcohol, whereas one would expect the ratio to be the same. He noticed that, using the reagent which he had proposed for the removal of aldehydes, the authors stated that higher results were, as a rule, obtained than with meta-phenylene-diamine hydrochloride. The result in the case of Experiment 4 in Table VII., however, was somewhat lower, and he thought that generally they were not very far apart. With regard to the experiments recorded in Table VIII., in which heating over a naked flame and on the water-bath for one hour were compared, the Allen-Marquardt figures in those cases were not given, but presumably there were very varying amounts of higher alcohols. With the naked flame the figures varied from 150 to 345, while on heating on the water-bath for one hour they all came out between 100 and 150. In order to be on the safe side he had generally, when he had used this method, heated for one hour on the water-bath, and he had obtained any number of figures between 100 and 150. The question of the removal of furfural was, of course, a very important one. In this connection the authors had mentioned the possibility of the formation of acridine dye-stuffs, which would be due probably to the formation of leuco-compounds, on which the strong sulphuric acid would act as an oxidizing agent. He had happened at one time to be interested in the acridines, and knew that they gave intensely coloured solutions.

Mr. CHAPMAN said that he, too, had been glad to hear that the authors proposed to extend their investigation to propyl alcohol. So far as his own experience had gone, whenever he had taken the precaution of determining the average molecular weight of the fatty acids by means of the barium salts, he had usually found this to indicate that they consisted almost entirely of butyric acid and valeric acid ; in other words, there was, as a rule, very little of the oxidation product of propyl alcohol. He thought, therefore, that very small proportions of propyl alcohol were extracted in this method, and if that alcohol was to be included under the heading of " higher alcohols " it seemed quite possible that the results hitherto obtained were not by any means accurate. He thought that the great importance of the authors' two communications on this subject lay in the fact that they had gone far to establish the superiority of the Allen-Marquardt method over the others they had investigated. The surface-tension methods, the Beckmann method, the colorimetric method, and the Rose-Herzfeld method had all been, or were being, severely discredited, and whatever errors might be inherent in the Allen-Marquardt process, it was at least based on scientific principles, and gave results which in the hands of different observers were capable of being compared.

Dr. SCHIDROWITZ, in reply, said that he was inclined to agree with Mr. Chapman that the examination of propyl alcohol would indicate that some of the results obtained in the past were not quite accurate. He agreed with Dr. Hewitt that the end-point in the titration with methyl orange had been a source of difficulty. At the same time he thought it might be well to continue to do it roughly, to see whether the ratio they had mentioned existed. In cases in which the ratio was found to be abnormal, a gravimetric estimation of chlorine should be carried out. This, however, would in practice only very rarely be necessary. The utility of the colorimetric method even as an index of quality was, he thought, very fallacious. He had known whiskies of the same class to show enormous differences by the colorimetric method, while there was little difference in the results obtained by the Allen-Marquardt method, and the whiskies themselves were very similar in flavour, body, and all the other qualities upon which commercial value depended. The impurities to which such differences were due, and which undoubtedly were bodies other than higher alcohols, might be present in small or in relatively large quantities ; but even if the quantities were relatively large, they were in many cases, in his opinion, insufficient to have any effect on the quality of the spirit. In the case in which Dr. Hewitt's reagent gave a low figure (namely, No. 4 in Table VII.) it was probable that there was only a very small quantity of these secondary constituents present, and that therefore the true value, as far as was possible by a colorimetric method, was obtained. At any rate, that reagent apparently took out the aldehydes and the furfural without doing anything else ; but even in the case referred to, the meta-phenylene-diamine reagent probably was the cause of some secondary reaction. With regard to the purification of amylic alcohol and butylic alcohol, they had described in their last paper the purification of amylic alcohol, and the same applied to butylic alcohol. But when different specimens of commercial iso-butylic alcohol were most carefully purified by the method referred to, even though the resultant

products displayed the same boiling-point, yet he knew from experience that their colorimetric properties were by no means necessarily identical; in fact, he had found wide differences.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

On the Amount of Alcohol in Bread. Otto Pohl. (*Zeits. angew. Chem.,* 1906, xix., 668.) -The author has investigated the statement of Balas (*Dingl. Journ.,* ccix., 399) that fresh (English) bread contains from 0·2 to 0·4 per cent. of alcohol. He distilled large quantities (over 4 kilogms.) of two kinds of German bread with water, and found the bread made from wheat-flour, using stale dough, contained 0·0744 and 0·0830 gram of alcohol per 100 grams bread, and bread made from the same flour, using yeast, contained 0·0508 and 0·0517 gram of alcohol per 100 grams bread. Besides the alcohol, which was identified beyond all doubt, he always obtained a small quantity of a heavy dark-brown oil, possessing the characteristic odour of new bread. A. G. L.

The Volumetric Determination of Casein in Milk. H. V. Arny and T. M. Pratt. (*Amer. Journ. Pharm.,* 1906, vol. 78, pp. 121-128.) -A definite quantity (5 to 30 c.c.) of the milk is treated with 20 c.c. of $\frac{N}{10}$ ferric alum solution (48·1 grams per litre) at the ordinary temperature, the mixture diluted with water, allowed to stand for a few minutes and filtered, the filter washed, and the excess of ferric alum in the filtrate washings (about 200 c.c.) determined by titration with potassium iodide, acid, and thiosulphate, the difference between the amounts taken and found giving the quantity required for precipitation of the casein. Experimental results quoted show that the method yields concordant results, and that the fat and sugar in the milk do not affect the reaction. In almost every case 10 c.c. of milk required 4 c.c. of the reagent (0·1924 gram of ferric alum) for precipitation of the casein. Numerous comparative determinations were also made to establish the relationship between the amount of nitrogen in the precipitate and the amount of ferric alum solution consumed. The nitrogen determined by Kjeldahl's method in the precipitates from 10 c.c. of six different milks ranged from 0·0322 to 0·0372 gram, and this corresponded to 2·05 to 2·32 per cent. of casein (factor 6·25), or 2·1 to 2·37 per cent. with the factor 6·38. The results of duplicate determinations were in close agreement. A deposit may form in the clear filtrate from the casein after the liquid has stood for some time, but this is due to ferric albuminate and not to casein, and the results of the titration are the same, whether the liquid be titrated whilst cloudy or after a second filtration. C. A. M.

A Rapid Method of Determining Fat in Cocoa. Tschaplowitz. (*Zeit. anal. Chem.*, 1906, xlv., 231-235.) Several grams of the finely-divided cocoa (sufficient to yield 1 or 2 grams of fat) are placed in a flask holding about 80 c.c., and having a long neck graduated from 73 to 77 c.c. in fifths of a c.c., and are boiled with 10 to 5 c.c. of alcohol, with constant shaking. The contents of the flask are then allowed to cool, 10 to 15 c.c. of ether introduced, and the mixture thoroughly shaken and boiled, after which it is cooled and made up to about 77 c.c. with ether, and the flask put aside. After about an hour or so the supernatant liquid will be sufficiently clear for 50 c.c. to be withdrawn with a pipette, a note being made of the total volume. This portion is evaporated in a porcelain basin on the water-bath, the residue taken up with a little warm ether and filtered through cotton-wool, the filtrate and washings evaporated, and the residue dried at 70° to 80° C., and finally for a short time at 100° C., and weighed. The deposit of fat-free cocoa in the flask has a density of nearly 1·6, and if 3 grams of cocoa were originally taken, 1 c.c. should be deducted from the total volume in the flask. The first boiling with alcohol appears to rupture the fat-cells completely. C. A. M.

Use of the Immersion Refractometer in the Determination of Caffeine. J. Hanus and K. Chocensky. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, vol. 11, p. 313-320.)—The strength of aqueous solutions of caffeine may be determined by means of the immersion refractometer (*cf.* ANALYST, 1903, xxviii., 91), as the refraction directly proportional to the quantity of caffeine present. At a temperature of 75° C. distilled water itself gives a scale reading of 15, and a solution containing 1 gram of caffeine in 100 c.c. of water a reading of 20. The amount of caffeine in 100 c.c. of solution may therefore be calculated from the formula,

$$x = \frac{y - 15}{5},$$

where y is the reading observed. A table is also given showing the amounts of caffeine corresponding with each 0·1 refractometer degree from 15 to 20.

W. P. S.

Determination of Sulphurous Acid in Meat. C. Mentzel. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, xi., 320-324.)—From the results given in this paper it is seen that meat itself, when acidified with phosphoric acid, distilled in an atmosphere of carbon dioxide, and the distillate oxidized with iodine and precipitated with barium chloride, never yields more than 0·002 per cent. of sulphur dioxide. The addition of onions to the meat (as is the case in some German potted meats) scarcely increases this amount, onions themselves only yielding 0·006 per cent. of sulphur dioxide when distilled under the above-mentioned conditions. The author concludes that meat or potted meat giving more than 0·004 per cent. of sulphur dioxide, or 0·005 per cent. in the case of samples flavoured with onions, must be considered as containing added sulphite preservative. W. P. S.

A New Method of Detecting Fluorine in Foods. J. Ville and E. Derrien. (*Bull. Soc. Chim.*, 1906, xxxv., 239-246.)—The method is based upon the fact that

sodium fluoride modifies the spectrum of methæmaglobin, producing a new one characterized by an absorption band in the orange-red to the right of the methæma-globin band. The reagent is prepared by mixing defibrinated ox-blood with four times its volume of a 0·1 per cent. solution of potassium oxalate, filtering the liquid, and dissolving a trace of potassium ferricyanide in 50 c.c. of the filtrate, in order to form methæmaglobin. In testing a liquid for fluorine, the reagent is added in the proportion of from 1 to 1·5 c.c. to 25 c.c. and the mixture examined with a spectroscope provided with a micrometer scale. In the case of wines the alcohol must be removed by evaporation, whilst red wines must be decolorized by means of precipitated manganese peroxide, which has also the effect of forming methæmaglobin in blood. Thus, on treating 25 c.c. of the filtrate with 0·1 gram of manganese peroxide, adding 1 to 1·5 c.c. of defibrinated blood mixed with four times its volume of 0·1 per cent. potassium oxalate solution, filtering, and examining the filtrate, the absorption spectrum is visible for about an hour when the wine contains from 0·08 to 0·1 gram of sodium fluoride per litre. It is rendered more pronounced and persistent by treating the wine successively with manganese peroxide and a solution of white of egg (to remove tannins) before adding the blood reagent. For the detection of fluorides in beer it is sufficient to test the liquid with the reagent after the removal of the alcohol and carbon dioxide, and the treatment with manganese peroxide and egg albumin is not required. Milk is examined by shaking 50 c.c. with about 4 c.c. of a 5 per cent. solution of oxalic acid, added drop by drop with constant shaking, heating the liquid for a few seconds on the water-bath, filtering it, and testing 25 c.c. of the filtrate with the reagent. As little as 0·05 to 0·1 gram of fluoride per litre of milk is readily detected, the characteristic absorption band remaining visible for several hours. In testing flesh foods a small portion of the sample is reduced to a pulp, and heated with a little water in a crucible on the water-bath. The process is repeated several times, the aqueous extracts cooled and filtered, and the filtrate mixed with the blood reagent and examined with the spectroscope. C. A. M.

A Dangerous Contamination of Phenacetin. C. Mannich. (*Ber. Deutsch. Pharm. Ges.*, xvi., 57; through *Pharm. Journ.*, 1906, lxxvi., 447.)—A sample of phenacetin that recently nearly caused the death of a patient was found to have a melting-point of 119° to 120° C. instead of 134° to 135° C. Further examination revealed the presence of 5·89 per cent. of chlorine in organic combination, and a substance was separated by digesting the sample with ether, evaporating the ethereal extract, and boiling out the residue with water. This substance proved to be *p*-chloracetanilide. Its occurrence in the sample could not be accounted for; it is not used in medicine, and is not formed during the preparation of phenacetin. The physiological action of *p*-chloracetanilide has not been determined, but the corresponding bromine compound, *p*-bromacetanilide, can be given internally with caution in doses of only 0·02 to 0·1 gram on account of the danger of producing collapse; *p*-chloracetanilide would probably act similarly. W. P. S.

The Alkaloids of Veratrum Album and their Determination. G. Brede-mann. (*Apoth. Zeit.*, xxi., 41; through *Pharm Journ.*, 1906, vol. 76, p. 283.)—The

rhizome and roots of *Veratrum album* (white hellebore) contain at least four alkaloids —viz., protoveratrine ($C_{32}H_{51}NO_{11}$), jervine ($C_{26}H_{37}NO_3$), pseudojervine ($C_{25}H_{43}NO_7$), and rubijervine ($C_{26}H_{43}NO_3$). Of these, the first is extremely toxic, jervine being weaker and the others non-toxic. The following method was employed for isolating the alkaloids: 5 kilogms. of the powdered drug were rendered alkaline with sodium hydroxide, exhausted with a mixture of equal volumes of ether and chloroform, and the ether-chloroform solution evaporated to a thin extract, which was extracted with dilute acetic acid. From the acid solution metaphosphoric acid precipitated the jervine and rubijervine. These were filtered off, and the filtrate made alkaline with ammonia and shaken out with ether, which extracted protoveratrine; it was then shaken out with chloroform, which removed pseudojervine. On treating the metaphosphate precipitate with sulphuric acid, rubijervine sulphate, being very soluble, was dissolved, leaving jervine sulphate as an insoluble residue. Commercial samples of the drug contained from 0·36 to 0·67 per cent. of total alkaloids. The alkaloids separated from three samples of the drug consisted of : Jervine, 0·102, 0·217, and 0·399 ; rubijervine, 0·053, 0·067, and 0·047 ; pseudojervine, 0·038, 0·032, and 0·027 ; protoveratrine, 0·062, 0·061, and 0·057 per cent. The mean neutralizing power of the alkaloids was found to be 0·00424 for each c.c. of $\frac{N}{2}$ acid, and the alkaloids may be determined volumetrically by adding 25 c.c. of $\frac{N}{2}$ acid to an aliquot part of the ether-chloroform solution, allowing about one-half the solvent to evaporate and titrating the excess of acid.

The following process may be used for the determination of the alkaloids in the tincture : 100 grams are evaporated to about one-half ; 1 gram of solid paraffin and 25 c.c. of water are added and the evaporation continued until all the alcohol is removed. Two grams of acetic acid are now introduced, and the mixture stirred, cooled, and filtered. The separated cake is again warmed with 20 c.c. of water and 1 gram of acetic acid and filtered. The united filtrates are rendered alkaline with sodium hydroxide, shaken out with ether-chloroform mixture, and the solution obtained titrated as described above. Commercial tinctures examined yielded from 0·024 to 0·063 per cent. of alkaloid. W. P. S.

Analysis of Nitroglycerine Tablets. E. Sautesson. (*Svenska Farm. Tids.*; through *Pharm. Journ.*, 1906, lxxvi., 109.)—One hundred tablets are weighed, powdered, and extracted with ether in a Soxhlet apparatus. The residue obtained on evaporating the ethereal solution consists of cacao butter and nitroglycerine; it is saponified with alcoholic potassium hydroxide solution, and the potassium nitrate yielded by the nitroglycerine reduced by nascent hydrogen, the ammonia produced being then determined in the usual manner. W. P. S.

The Examination of Formaldehyde Pastilles. Ernst Rüst. (*Zeits. angew. Chem.*, 1906, xix., 474.)—The "formaldehyde pastilles" (trioxymethylene), used for disinfecting purposes, should weigh as nearly as possible 1 gram each, be practically completely soluble in hot water, and give a neutral solution. When tested by Blank and Finkenbeiner's method they should yield 95 to 97 per cent. of formaldehyde. Pastilles with only 85 per cent. of formaldehyde are found in commerce. They

should be tested for carbonaceous residue by heating 10 grams in a platinum dish over a burner until they take fire, when they are allowed to burn themselves out without further heating; the residue should not exceed 0·1 per cent.; pastilles with a 0·5 per cent. residue are absolutely useless. The residue obtained should be examined for ash, which should not exceed 0·05 to 0·08 per cent., and give a neutral or only faintly alkaline reaction. The gases given off during the burning should also be observed, as the author has found pastilles which evolved what was apparently chlorine during the heating.   A. G. L.

Effects of Borax and Boric Acid on the Human System : A Critical Review of the Report of Dr. H. W. Wiley. O. Liebreich (Pamphlet.)—The author reviews and criticises Dr. Wiley's report (*cf.* ANALYST, 1904, xxix., 357) on the effect of borax administered with food. From an exhaustive examination of the figures and reports, he concludes that no injurious effects were produced by the administration of the boron preservatives, and considers that the symptoms of ill-health noticed during the experiments must be attributed to inefficient hygienic conditions, to an injudicious mode of administering the preservative, and in a few cases to an unsuitable choice of persons for the experiment. The slight loss of weight of some of the men may be explained by chance occurrences at the preservative table; moreover, a loss of weight does not by any means always indicate an injurious influence. Liebreich also claims that the experiments on metabolism were undertaken with no equilibrium of nutrition, and that the fore periods were too short to prove regularity in feeding. As the percentages of nitrogen and phosphoric acid in the food were constantly changing, it is impossible to decide whether the excretion increased during the preservative period. He also considers that the medical supervision was insufficient, and that the situation of the dining-room left much to be desired.   W. P. S.

ORGANIC ANALYSIS.

Quantitative Determination of the Carbonyl Group in Aldehydes, Ketones, etc. Watson Smith, Jun. (*Chem. News*, vol. 93, p. 83.) The method is a modification of that of Strache, in which the aldehyde or ketone is mixed with an excess of phenylhydrazine, the excess oxidized by boiling with Fehling's solution, and the nitrogen gas liberated, collected, and measured. From 0·1 to 0·5 gram of the substance is mixed with 1 part, accurately measured, of a 5 per cent. phenylhydrazine solution, and 1·5 parts of a 10 per cent. sodium acetate solution, in a 100 c.c. measuring-flask. The bulk is made up with water to about 50 c.c. and heated on the water-bath for fifteen minutes, then cooled, diluted to 100 c.c., well shaken, and 50 c.c. pipetted into the dropping funnel, C, the stem of which is first filled with water. The end of the funnel is drawn out into a hook-shaped capillary, and dips down to the bottom of the flask, to prevent the collection of bubbles of gas. The flask has a capacity of 750 to 1,000 c.c., and contains 200 c.c. of Fehling's solution, on the surface of which floats a thin layer of paraffin wax. Between the flask and the nitrometer are a reflux condenser, to prevent any liquid distilling over, and an absorption apparatus, E, which removes the benzene vapour. Several

substances have been tested as to their suitability as absorbing material for charging the apparatus, E, including paraffin oil and wax, caoutchouc, sulphuric acid, and a mixture of sulphuric and nitric acids in molecular proportions, the last being found to give the best results. The contents of the flask are first heated, while a current of well-washed carbon dioxide passes from the Kipp's apparatus through the flask and absorption bulbs to the nitrometer until the bubbles of gas rising in the latter
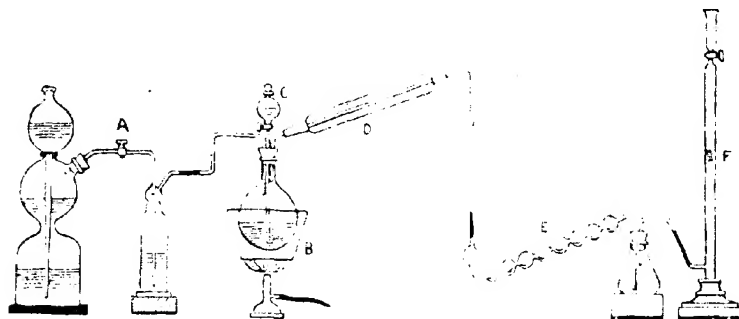

are sufficiently small to be negligible. The solution in the funnel is then allowed to mix with the Fehling's solution, and the funnel rinsed out once or twice with hot water. The gas evolved by the reaction between the Fehling's solution and phenyl-hydrazine is carried along by the carbon dioxide through the absorption apparatus into the nitrometer, which is filled with potassium hydroxide solution (1 in 1). As soon as the bubbles have become as small as before the nitrometer is disconnected, allowed to stand some time, and the gas volume read off and reduced to 0° C. and 760 mm. Immediately prior to the actual experiment with the aldehyde or ketone a blank determination is made with the phenylhydrazine solution alone, 10 c.c. of which, with the requisite quantity of sodium acetate solution, is diluted to 100 c.c., and 50 c.c. pipetted into the dropping-funnel, and the process carried out as described above. The amount of nitrogen evolved in the actual determination deducted from the blank gives the volume of nitrogen equivalent to the phenylhydrazine used in forming a hydrazone with the aldehyde, 1 c.c. of nitrogen being equivalent to 0·001252 gram of CO. W. H. S.

Novel Reactions of Aceto-acetic Acid. E. Riegler. (*Münchener medizin. Wochenschr.*, 1906, vol. 53, p. 448; through *Chem. Zeit.*, 1906, xxx. [*Rep.*], 122.)— Arnold's diazo reaction is best carried out as follows: 20 c.c. of the urine are well mixed with 4 or 5 drops of concentrated hydrochloric acid and 10 c.c. of ether, 1 c.c. of a solution of 1 gram of *p*-amino-acetophenone and 5 c.c. of hydrochloric acid in 100 c.c. of water, 1 c.c. of a 0·5 per cent. sodium nitrite solution, and, after well shaking, 10 drops of 10 per cent. ammonia are added. After again shaking, the ethereal solution is separated; one part is evaporated to dryness, and the residue treated with 5 to 6 drops of hydrochloric acid; the remainder of the ethereal solution is shaken with concentrated hydrochloric acid. In both cases a fine bluish-violet

colour is obtained if aceto-acetic acid was present in the urine. This colour is due to diazo-acetophenone diacetic acid—

$$CH_3.CO.C_6H_4.N:N.CH{\diagup}^{CO.OH}_{CO.CH_3},$$
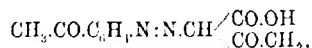
a brown substance, insoluble in water, soluble in chloroform, alcohol, and ether. From its alcoholic solution this substance crystallizes in fine violet microscopical crystals.   A. G. L.

Detection and Determination of Nitrotoluene in Nitrobenzene and of Toluene in Benzene. P. N. Raikow and E. Urkewitsch. (*Chem. Zeit.*, 1906, xxx., 295.)—The authors have found that potassium hydroxide forms a brown compound with both nitrotoluene and nitrobenzene, whilst sodium hydroxide reacts only with nitrotoluene. Rubidium hydroxide behaves similarly to potassium hydroxide, and lithium hydroxide resembles sodium hydroxide in its action, which is, however, less marked. Nitrotoluene can consequently be distinguished from nitrobenzene by treating it with sodium hydroxide. The test is best carried out by placing 0·5 gram of powdered sodium hydroxide and 1 c.c. of gasoline in a test-tube and allowing a small drop of the liquid to be tested to flow down the side of the tube. Even 0·00025 gram of nitrotoluene will produce a brownish colour, which may change to gray, reddish, or even blue in a few minutes, and is quite unaffected by any nitrobenzene present. By comparing the colour obtained with that given by a known amount of nitrotoluene the quantity of the latter may be determined with some degree of exactness.

Benzene may be examined for toluene by testing the nitrated oil as above. The authors find that it is practically impossible to remove toluene completely from benzene by fractional crystallization, but that pure benzene can be obtained by fractional nitration, toluene being more readily nitrated than benzene.

                                                                 A. G. L.

The Determination of Suspended Water in Naphtha by Means of Wyleshinski's Centrifugal Machine. K. Charitschkow. (*Westnikshiro w. weschtsch.*, 1905, vol. 6, p. 187; through *Chem. Zeit.*, 1906, xxx. [*Rep.*], 93.)—Very accurate determinations of the suspended water in naphtha can be made by mixing the sample with its own volume of benzene and then treating in Wyleshinski's centrifugal machine. The results are always a little higher than those obtained by diluting the sample with benzene and allowing the water to settle out of its own accord.   A. G. L.

The Bromine Absorption of Oil of Turpentine. W. Vaubel. (*Zeit. öffentl. Chem.*, 1906, xii., 107, 108.)—The following is an improvement on the author's original method of determining the bromine absorption of oils of turpentine: From 1 to 2 grams of the sample are dissolved in chloroform, about 100 c.c. of water, 5 grams of potassium bromide, and 10 c.c. of concentrated hydrochloric acid are added, and the mixture then titrated with a standardized potassium bromate solution until it

.hows the yellow colour of free bromine. The absorption of bromine is at first rapid, but becomes slower towards the end of the reaction ; the bromate solution should be added until the coloration persists for half an hour. American oil of turpentine, according to the results given, has a bromine absorption of from 220 to 230, French 210. quantities approximating to that required for the formation of the tetrabromide, whilst pinene has an absorption of 251. As is shown in the author's table, turpentines are met with which nearly approach this last number ; more generally they have absorption numbers of from 220 to 230 ; hence commercial turpentines contain from 86 to 90·5 per cent. of pinene, or some body having a similar bromine absorption. Many adulterants contain no pinene. Since some of the American turpentines polarize to the left, and the amount or kind of rotation gives no sufficient criterion as to their purity or otherwise, there only remains as reliable the bromine absorption test.   W. P. S.

Linaloe Oil. E. J. Parry and C. T. Bennett. (*Chemist and Druggist*, 1906, xviii., 544.)—The authors have examined a number of samples of this oil obtained from the most trustworthy sources, and consider that the following figures fairly represent the analytical data yielded by the best quality of linaloe oil:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Specific gravity at 15° C.	0·882	0·884	0·882	0·882	0·887	0·879
Optical rotation	− 13°	− 11°	− 11°	10°	− 11°30′	− 12°10′
Esters	11·2%	5·8%		5·5%	5·8%	5·5%
Linalol	57%	56·2%		63%	66%	65·5%

At least 55 per cent. of the oil should distil between 195° and 205° C., whilst usually over 60 per cent. is obtained. The optical rotation of the main fractions obtained from genuine oils scarcely differs from that of the oil itself, whilst the fractions yielded by adulterated samples possess widely differing rotations. The authors do not propose definite standards, but think that the above-mentioned figures may be of assistance in judging the purity of a sample of linaloe oil.

                                                                                              W. P. S.

Examination of Rosin Oil. Utz. (*Chem. Rev.*, 1906, xiii., 48 ; through *Chem. Zeit.*, 1906, xxx. [*Rep.*], 108.)—The author has examined a number of methods for the detection of mineral oils in rosin oils. He finds that the acetone method is useless for small quantities (5 to 10 per cent.) of mineral oil. Finkener's method (*Zeits. anal. Chem.*, 1887, 652) gave better results, 1 volume of rosin oil being soluble in at most 17 volumes of a mixture of 10 volumes of alcohol (specific gravity 0·8182 at 15·5° C.) and 1 volume of chloroform, whilst 1 volume of mineral oil does not dissolve even in 100 volumes of the mixture. Carbon tetrachloride cannot be used to separate the two kinds of oils, both being soluble in it. Holde's method (*Zeits. angew. Chem.*, 1891, 588) is useful. It consists in shaking the oil at the ordinary temperature with 96 per cent. alcohol, and determining the refractive index

of the undissolved oil. Small quantities of mineral oil may be completely dissolved by the alcohol, but can be separated again by adding a little water. The presence of mineral oil lowers the refractive index so much that 1 per cent. of any mineral oil, excepting petroleum, can still be recognised in this way. The author believes it possible to work out a method which depends on treating the oil with concentrated and fuming sulphuric acid, and then determining, the refractive index of the residual oil.   A. G. L.

On the Use of Dimethyl Sulphate for the Detection and Determination of Coal-tar Oils in Mixtures with Rosin Oils and Mineral Oils, and on its Behaviour towards Fatty Oils, Spirits of Turpentine and Pinoline. E. Valenta. (*Chem. Zeit.*, 1906, xxx., 266.)—The author has found that dimethyl sulphate dissolves aromatic hydrocarbons, such as occur in coal-tar, in all proportions, whilst it neither dissolves, nor is soluble in, paraffin hydrocarbons or rosin oils. Consequently, the quantity of coal-tar oils added to mineral oils or rosin oils may be rapidly determined by simply shaking up the sample with one and one-half times its volume of dimethyl sulphate in a stoppered measuring cylinder, and noting the increase in volume of the dimethyl sulphate. The results obtained are accurate to 1 or at most 2 per cent. If desired, the oil can also be weighed by separating, destroying the dimethyl sulphate by saponification, and collecting the residual unsaponifiable oil as usual. Coal-tar oils may also be determined in a similar way in printing and lithographic inks, which contain linseed oil, rosin, etc., by first separating the pigment as usual, then saponifying with alcoholic caustic soda, extracting the unsaponifiable matter with ether, and treating it with dimethyl sulphate as above.

Dimethyl sulphate also dissolves substances such as nitrobenzene, nitro-naphthalene, etc., used as deblooming agents for mineral oils, and may be used for their extraction. On mixing dimethyl sulphate with fatty oils (olive, almond oils), its volume diminishes. The contrary is the case with pinoline and spirits of turpentine, about 30 per cent. of these bodies being dissolved in the dimethyl sulphate. Pinoline yields an orange solution in the cold; on heating, it dissolves completely, forming a dark-gray liquid; the mixing is unaccompanied by any rise in temperature. Turpentine gives a colourless solution and a marked rise in temperature. Dimethyl sulphate possesses toxic properties, and should not be handled too freely.   A. G. L.

The Examination of Raw Caoutchouc. W. Esch. (*Gummi Zeit.*, 1906, vol. 20, p. 494; through *Chem. Zeit.*, 1906, xxx. [*Rep.*], 101.)—The raw caoutchouc is separated by testing with the finger into firm elastic and soft or tarry. Dirt and impurities should be looked for both with the naked eye and a lens, and it should be remembered that a quantity of dirt which would absolutely condemn the use of a soft tarry kind for many purposes can be easily washed out of a firm elastic variety. Cuts should be made in the rubber, and the colour noted; it should be lighter than that of the exterior. If moisture or serum ooze out, they should be tested to see whether they will yield caoutchouc. Failure to do this indicates a faulty coagulation of the sample.

The author insists that the actual chemical examination *must* be made on the

.ished and dried samples only, not on the raw caoutchouc, and gives some further
details concerning his and Chwolles' method. A. G. L.

The Volumetric Determination of Uric Acid. A. Ronchèse. (Journ. Pharm. Chim., 1906, xxiii., 336-340.)—Uric acid is oxidized by iodine at the ordinary temperature in a medium rendered alkaline by potassium bicarbonate, borax, or other substance without action upon iodine, each molecule of uric acid requiring two atoms of iodine. Thus each c.c. of $\frac{1}{10}$ iodine solution is equivalent to 0·0084 gram of uric acid. In using the method with urines, it is necessary to separate the uric acid from other bodies that might act upon the iodine—e.g., by precipitating it as ammonium urate in the following manner: 100 c.c. of the urine are treated with 15 c.c. of ammonium hydroxide and 15 grams of ammonium chloride, and the mixture allowed to stand for thirty minutes. The precipitated urate is collected and washed with a solution containing 150 c.c. of ammonium hydroxide and 150 grams of ammonium chloride per litre, and then suspended in 300 c.c. of water and dissolved by the addition of dilute acetic acid. The solution is now rendered strongly alkaline by the addition of 20 c.c. of a saturated solution of potassium bicarbonate or borax, and titrated with a $\frac{1}{10}$ solution of iodine. The number of c.c. used, multiplied by 0·084, plus 0·01 gram (the correction for the solubility of the precipitate during the washing), gives the amount of uric acid per litre. The results thus obtained are in close agreement with those given by the Salkowski-Ludwig method. The presence of albumin has no appreciable effect upon the determination. C. A. M.

The Determination of Small Quantities of Ammonia in the Presence of Urea. Frenkel. (Bull. Soc. Chim., 1906, xxxv., 250, 251.)—The drawback of Schlosing's method of liberating the ammonia by means of calcium hydroxide in the cold is that as long as sixty hours are required for complete absorption of the ammonia in the standard acid. The author, however, finds that a determination can be made in two hours by passing a current of air through the flask, the air itself having first been freed from ammonia by passage through sulphuric acid, and from carbon dioxide by passage through potassium hydroxide solution. Test results quoted show that the whole of the ammonia is expelled from the solution under examination within two hours, and that no fresh ammonia is produced from the urea. C. A. M.

Rosin Size Analysis. Clayton Beadle and Henry P. Stevens. (Chem. News, 1906, vol. 93, p. 155.)—In the usual method of determining moisture in rosin size, which consists in determining the loss in weight when the size is heated in a flat dish or clock-glass at 100° to 110° C., any spirit of turpentine left in the rosin may volatilize and cause too high a result. To see whether this error is serious, the authors have determined the moisture in other ways: (1) The size was heated in a glass flask placed in an air-bath; the flask was connected to a condensing tube, the end of which was bent down and dipped for a short distance into a burette previously filled up to the 50 c.c. mark with water; the volume of water distilled over, as well

as that of the turpentine, was directly read off. (2) The loss in weight of the flask used in method (1) was noted. (3) Water was determined by difference after determining total rosin, total soda, turpentine, and other mineral matter in the size. The mean values obtained by the different methods on a sample of size containing 0·31 per cent. of turpentine were : (1) 38·75, (2) 39·55, (3) 39·31 per cent. of moisture. The usual method gave 39·5 per cent. The authors infer that for samples of size containing only small amounts of turpentine the usual method is sufficiently accurate.

A. G. L.

On Methods of Distinguishing between the Pitch from Brown Coal-tar and other Pitches. E. Graefe. (*Chem. Zeit.*, 1906, xxx., 298.)—Pitch from brown coal-tar, including both the " goudron " left by the distillation of the tar and the acid-pitch obtained in the purification of the distillates with sulphuric acid and soda, can be distinguished from most other kinds of pitch by its high content of phenols. This may be easily recognised by boiling 0·2 to 0·5 gram of the pitch with 5 to 10 c.c. of normal sodium hydrate solution, filtering, and adding to this solution a few drops of a solution of diazo-benzene chloride. The appearance of a red colour or precipitate indicates the presence of phenols. Pitch from wood-tar also contains an appreciable quantity of phenols, but may be recognised by the acidity of the vapours given off on distillation and by the incomplete solubility in benzene.

For the determination of the melting-point of pitches fusing at a high temperature (200° C.), the author modifies Krämer and Sarnow's method as follows : One end of a melting-point tube is closed by a cork ; the usual quantity of pitch is then placed in the tube and covered with a layer of 5 grams of mercury. The pitch is melted over a naked flame or in a paraffin bath, and allowed to cool. The cork is then removed, and the tube heated as usual in a bath of paraffin, the layer of air below the pitch protecting the latter from the solvent action of the paraffin on it.

A. G. L.

Examination of Paints. J. R. Moechel. (*Chem. Trade Journ.*, 1906, xxxviii., 235.)—Of twenty tests, the first eight, which were applied to plates of glass, wood, tin-sheeting, galvanized iron, or sheet steel, 1 inch by 3 inches or 2 inches by 5 inches, coated with the paint and allowed to dry for eight days at the ordinary temperature, determine the resistance to various reagents—viz. (1) *acids*, by immersion in 10 and 25 per cent. HCl, H_2SO_4, and HNO_3, for twenty-four hours at room temperature, and a second series for two hours on the water-bath ; (2) *acid fumes*, by allowing the fumes of hot HCl, H_2SO_4, and HNO_3 to play directly on the paint for three minutes ; (3) *alkalies*, by immersion in 10 and 25 per cent. NaOH, both at room temperature, and on the water-bath for fifteen minutes, noting appearance after standing one hour : (4) *ammonia fumes*, by blowing air for five minutes into a wash-bottle one-fourth full of strong NH_4OH, having a short stem funnel through the cork, on which is laid the painted surface ; (5 and 6) *sulphurous fumes* and *hydrogen sulphide*, by treating the painted surface for thirty minutes with SO_2 or H_2S, as described with NH_4OH ; (7) *steam under pressure*, by exposure for one hour at 18 to 20 inches from the boiler safety-valve ; and (8) *free steam*, by subjecting for twelve hours to steam from a

water-bath. The *spreading* and *covering capacities* are measured respectively by the amount of paint used, and the number of coats required to obtain opaqueness. The *rust-preventing power* is determined by applying a double coat to plates of sheet-iron, thoroughly polished with a dry powder, allowing to dry for eight days, and then loosening the coat of paint by placing the plates face downwards upon a boiling water-bath for about twelve hours, drying with filter-paper, and finally for one hour at 100 C., employing a little $CHCl_3$, if necessary, to help loosen the edges. With good paints no rust should be found on the polished metal. *Time of drying* should be observed, and the *elasticity* tested by bending and rebending painted strips of tin sheeting and thin, flexible drawing-paper, covering them with a glass plate, and weighing down for twenty-four hours with a block weighing 3 to 5 pounds. The *penetration into wood* is ascertained by applying two coats of paint to strips of white pine-wood, some air-dried, others dried in the water-oven for three hours, cutting the strips crosswise and lengthwise, and examining the sections with a good lens, and the power of *preventing absorption of water* by painting air-dry blocks of the material to be rendered waterproof, weighing them, and then boiling in distilled water for thirty minutes, drying with blotting-paper, and again weighing. *Adhesion* of the paint is tested by applying a vacuum to the surface, and the *fineness of pigment* by placing a small amount upon a glass plate, pressing down with another glass plate, standing both plates on end and allowing the paint to run, when, after one hour, no separation of pigment particles should appear for at least an inch of downward surface. The exact *shade and tint of colour* are examined by comparison with standards on micro scopic glass slides, the two colours being placed side by side just touching each other, and viewed first over a white, then over a black surface. Finally, the effects of *dry heat* and of a *naked flame* are observed, the former by subjecting painted glass, wood, or metal plates to temperatures of 100°, 300°, 500° C., for one hour each, and the latter by exposing the painted surface to various gas-burners, of approximately known temperatures, for periods of one, two, and three minutes. W. H. S.

INORGANIC ANALYSIS.

On the Iodometric Determination of Copper. Paul Gerlinger. (*Zeits. angew. Chem.*, 1906, xix., 520.)—In order to obviate the uncertainty of the end-point in the iodometric determination of copper due to the presence in the liquid of a large precipitate, the author adds a sufficiently great excess of potassium iodide to redissolve the whole of the cuprous iodide first precipitated. For 0.2 gram of copper, at least 10 grams of potassium iodide (added in the powdered state) are necessary, and the bulk of the liquid should be kept low. He also finds it unnecessary to boil the liquid after the neutralization of the acid liquid by ammonia, as recommended by Low, provided no lower oxides of nitrogen are present. Working on pure copper solutions, the author obtained very exact values by his method. A. G. L.

On the Determination of Copper as Thiocyanate. Ernst Murmann. (*Oesterr. Chem. Zeit.*, 1906, ix., 67.)—The author has obtained good results by weighing the cuprous thiocyanate dried at 100° C., in a Gooch crucible. Large excesses of

thiocyanate and of sulphurous acid should be avoided, and the precipitate should be washed first with a liquid containing potassium thiocyanate and sulphurous acid, and finally with a little alcohol.   A. G. L.

Detection of Traces of Copper in Distilled Water. K. Ebert. (*Apoth. Zeit.*, 1905, xx., 908; through *Pharm. Journ.*, 1906, lxxvi., 387.)—About 500 c.c. of the water are treated with a few drops of ammonia, and then filtered three times through a plug of cotton-wool. A faint green colour on the cotton-wool indicates the presence of copper in quantity too small to be detected by hydrogen sulphide or potassium ferrocyanide.   W. P. S.

Comparison of Wet and Dry Assay of Gold Telluric Ores. W. F. Hillebrand and E. T. Allen. (*Chem. News*, 1906, vol. 93, pp. 100, 101, 109-111, 121, 122, and 132-134.) Working with ores containing 0·07 to 0·09 per cent. tellurium and 0·05 to 0·06 per cent. gold, the authors find that, provided slag and cupel losses are corrected for, fire assay by crucible gives results equal to those obtained by precipitating the gold by ferrous sulphate, after extracting with nitric acid, filtering, adding bromine water, evaporating nearly to dryness, digesting the residue with HCl, and evaporating two or three times with further quantities of HCl. An investigation of the errors occurring in fire assaying and parting, made on proof gold and silver from the United States Mint, has shown that the slag loss is very small, as is also the cupellation loss by volatilization except at high temperatures. The loss of gold by absorption is considerable, being largely influenced by slight changes in temperature, and greater with pure gold and alloys poor in silver than with those containing much silver. A higher temperature at the end of cupellation with gold beads than with silver is unnecessary, the most exact results being obtained when feather litharge was still abundant at time of brightening, and nothing is gained by leaving gold beads in the muffle for some time after brightening in order to remove last traces of lead. The error due to retention of lead in the beads is important, 0·30 and 0·37 per cent. of lead being found respectively in two cases. Silver is completely removed from quartation alloys by nitric acid, but only after three or more extractions. Admixture of pure nitrous acid with the nitric acid used in parting has no appreciable effect, and any slight trace of gold dissolved by pure nitric acid is negligible.   W. H. S.

On the Separation of Tungsten from Tin. Ed. Donath. (*Zeits. angew. Chem.*, 1906, xix., 473.)—The recent publication of Angenot's process (ANALYST, this vol., p. 84) has induced the author to call attention to his own previously described and simpler method of effecting this separation. The mixture of stannic oxide and tungsten trioxide is heated to redness for fifteen minutes with zinc dust or filings in a covered porcelain crucible. The porous mass obtained is transferred to a beaker and warmed with dilute hydrochloric acid (1 to 2) until all the tin has dissolved, when the liquid is cooled somewhat and cautiously treated with powdered potassium chlorate until the blue tungsten oxide has been completely oxidized to yellow tungstic acid. After diluting the liquid with at least one and one-half times its volume of
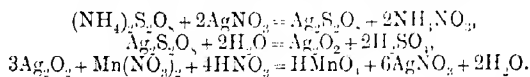
water, it is allowed to stand for twenty-four hours, when the tungstic acid is filtered off, washed first with water containing nitric acid, then with water containing ammonium nitrate, ignited and weighed. If necessary, tin can be determined, as usual, in the filtrate.   A. G. L.

The Direct Titration of Zinc by Means of Potassium Ferrocyanide.   E. Murmann. (*Zeit. anal. Chem.*, 1906, xlv., 174-181.)—The drawback of the ordinary method in which the end-point of the reaction is determined by " spotting " can be obviated by adding 2 to 5 c.c. of a 1 per cent. solution of uranyl chloride to the hot solution (100 to 150 c.c.). The change of colour from brown to bluish-gray is very sharp when the solution is nearly boiling, and 0·1 c.c. of the ordinary zinc solution (0·01 gram per c.c.) is sufficient to produce it when the excess of potassium ferrocyanide is titrated back. The ferrocyanide solution is prepared by dissolving 43·11 grams of the pure crystalline salt in a litre. Experiments to determine the influence of salts and acids showed that considerable quantities of salts, including ammonium chloride, cause only a slight increase in the amount of potassium ferrocyanide consumed, and that the effect of hydrochloric acid is also small, provided its quantity does not exceed 20 c.c. of specific gravity 1·075) to 100 to 150 c.c. of liquid. Free nitric acid must not be present, and it is therefore advisable to use uranyl chloride instead of uranyl nitrate. For the determination of zinc in zinc blend, 2·5 grams of the sample are dissolved in hydrochloric acid with the addition of a little nitric acid, the solution filtered, evaporated with sulphuric acid, filtered, treated with hydrogen sulphide, filtered, and oxidized with bromine. It is then filtered into a 500 c.c. flask containing 100 c.c. of ammonia solution and 10 c.c. of concentrated ammonium carbonate solution, again filtered, and finally made up to the mark. A definite quantity is taken, treated with 5 c.c. of the uranyl chloride solution, and, after neutralization, with 10 c.c. of hydrochloric acid (specific gravity 1·075) titrated at an almost boiling temperature.

                                                                                   C. A. M.

The Determination of Manganese in Cast Iron and Steel.   O. Brichant. (*J. u. de Chim. anal.*, 1906, vol. 11, pp. 124-127.)—The following modification of Schmidt's ammonium persulphate method is recommended as the most suitable for laboratory work. It is based upon the conversion of the manganese into permanganic acid by ammonium persulphate in the presence of silver nitrate :

$$(NH_4)_2S_2O_8 + 2AgNO_3 = Ag_2S_2O_8 + 2NH_4NO_3,$$
$$Ag_2S_2O_8 + 2H_2O = Ag_2O_2 + 2H_2SO_4,$$
$$3Ag_2O_2 + Mn(NO_3)_2 + 4HNO_3 = HMnO_4 + 6AgNO_3 + 2H_2O.$$

(*a*) *Steels.*—One gram of steel filings is dissolved in nitric acid of specific gravity 1·135, and the solution diluted with sufficient cold water to bring the temperature to about 50° C., and then treated with 10 c.c. of a $\frac{N}{10}$ solution of silver nitrate and about 0·2 gram of ammonium persulphate, and heated until the rose colour disappears. The liquid is then decolorized with ferrous sulphate solution, cooled to about 60° C., treated with a fresh portion of ammonium persulphate, shaken, and allowed to stand for about ten minutes. The whole of the manganese will then have

been converted into permanganic acid, and the liquid, when cold, is titrated w.. standard sodium arsenite solution until the violet colour disappears.

(*b*) *Cast Iron containing less than 2 per Cent. of Manganese.*—One gram . dissolved in 25 c.c. of nitric acid, the solution diluted with cold water and filter. from silica and graphite, and the manganese determined as in the case of steel.

(*c*) *Spiegel and Ferro-Manganese.*—One gram is dissolved, the solution made to 250 or 500 c.c., and the manganese determined in 25 or 50 c.c., after the additi of 25 c.c. of nitric acid.

The sodium arsenite solution is prepared by dissolving 0·9 gram of arseni. acid and 3 grams of sodium bicarbonate in 250 c.c. of water and diluting the solut: to a litre. It is standardized by dissolving 0·278 gram of manganese dioxide . 15 c.c. of strong hydrochloric acid, adding 2 to 3 c.c. of strong sulphuric acid a. evaporating the solution until the appearance of white fumes, after which it . cooled and made up to a litre with water. Fifty c.c. of this solution (=0·01 gr. of manganese) are treated with 10 c.c. of silver nitrate solution (17 grams per litr. 25 c.c. of nitric acid (specific gravity 1·20), and about 1 gram of ammonium p. sulphate, and the whole heated to about 60° C., cooled, and titrated. The meth. is stated to be more rapid than the expensive bismuth tetroxide method, and to yie. very accurate results.   C. A. M.

Derangement of a Public Water-Supply by Manganese Sulphate. R. Woy. (*Zeit. öffentl. Chem.*, 1906, xii., 121-125.)—Up to the beginning of the ye. 1905 the town of Breslau, Silesia, had been supplied with water drawn from t: river Oder and filtered through gravel. From that time, however, a new a. apparently more satisfactory supply was obtained from the surrounding country, t: use of the filtered river-water being abandoned. About March 28 of this year . extraordinary change in the character of the water was noticed, the peculiarity fir: noticed being an unpleasant taste. On analysis the water was found to have . slightly acid reaction, and to contain a considerable quantity of manganese. t: normal amount of sulphates in the water also showing an increase. The quantity . manganese present varied from day, the maximum found being 0·109 gram of ma: ganous oxide (MnO) per litre. The source of the manganese salts has not yet be. investigated.   W. P. S.

On the Quantitative Determination of Cyanate in the Presence of Cyanide. Wilhelm Wild. (*Zeits. anal. Chem.*, 1906, vol. xlix., p. 122.)—Confirm: . Ewan's statement (*Journ. Soc. Chem. Ind.*, xxiii., 244), the author finds that t: solubility of silver cyanate in pure water is very considerable, amounting 0·0075 gram in 100 c.c. of water at 22° C. In solutions containing excess of silve: nitrate, however, the solubility is very much less, being only 0·0006 gram in 100 c. of approximately $\frac{N}{100}$ silver nitrate solution. He consequently proposes to deter::: cyanate in the presence of cyanide by precipitating with an excess of standard silve: nitrate in neutral solution, making the liquid up to a definite volume, and titrati: the excess of silver present in an aliquot part of the filtered solution. On anoth: portion of the sample the cyanide only is determined by precipitation with silve:

...rate in nitric acid solution, the difference between the two values being taken as ... to cyanate. Any carbonate present in the sample is removed by calcium nitrate ...ore making the first titration. A. G. L.

The Preparation of Pure Chloric Acid for Analytical Purposes. V. Bernard. (*Ann. de Chim. anal.*, 1906, vol. 11, pp. 81, 82.)—A solution of 800 grams of pure barium chlorate in 1,700 c.c. of water is treated with 213 grams of pure sulphuric acid (60° Bé.) added little by little, whilst the flask is cooled in a current of water to prevent the liquid becoming hot, with the consequent formation of perchloric acid. The barium sulphate is removed by filtering the liquid through purified asbestos with the aid of a pump, and the almost colourless filtrate (1,750 c.c.) can be used for oxidizing purposes in the place of nitric acid or potassium chlorate. It has the advantage of being decomposed without residue in the presence of hydrochloric acid. C. A. M.

APPARATUS.

New Form of Calcium Chloride Tube. A. E. Hill. (*Proc. Chem. Soc.*, 1906, vol. 22, p. 87.)—The apparatus consists essentially of an inner exit tube, A, fused into a larger tube, B, which has a side-tube, E, provided with the usual form of bulb. Both tubes are filled from the bottom, G, with finely-granulated calcium chloride, above and below which are placed plugs of glass wool, and the whole closed with a cork, which is cut off flush with the bottom of the tube and covered with sealing-wax. The space in B, above the side-tube, E, is left empty, to allow diffusion of the water vapour before it comes in contact with the calcium chloride, thus insuring uniform wetting of the latter. The advantages of the tube are (1) a double scrubbing action obtained with a comparatively small amount of calcium chloride; (2) its compactness and strength, there being no fragile bend, as in a U-tube; and (3) the ease of emptying and refilling, and of drying before weighing. The apparatus is manufactured by Baird and Tatlock, who have registered the design.
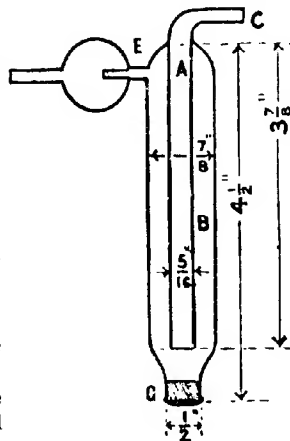
W. H. S.

Magnesia Apparatus at High Temperatures. E. Wedekind. (*Chem. Zeit.*, 1906, xxx., 329.)—The author gives the results of some experiments on the behaviour at high temperatures of articles made of magnesia supplied by the Royal Berlin Porcelain Factory. He found that they stood the action of the electric arc well, fusing only at the parts actually touched by the arc, but would not stand in fused thermite. They also require careful heating and cooling if they are not to crack. The author believes that magnesia articles will not come into general use owing to their high

price, coupled with the fact that as a rule they can only be used once, as fused substances adhere to them. For experiments with the arc he strongly recommends blocks of magnesite bound with iron, as supplied by the Frankfurter Gold und Silberscheideanstalt. These may be used up to sixty times before being destroyed.

A. G. L.

Delivery Funnel for introducing Liquids under Increased or Diminished Pressure. T. J. Bryan. (*Journ. Amer. Chem. Soc.*, 1906, xxviii., 80.)—Three

forms of funnel are described, the principle being the same in each—viz., that on opening the tap the pressure on the upper and lower surfaces of the liquid in the funnel shall be the same, whether greater than that of the atmosphere, due to increase of pressure in the generating flask, or less, as in fractional distillation *in vacuo*.

Fig. 1 shows a dropping funnel, whose tube, B, which should be of small bore, and not exceed 4 inches in length, passes through and is sealed to the tube, A, at E, the side-tube, C, with a glass tap at D, being fused into the funnel at K, and into the tube, A, at F. The funnel has an air-vent in the stopper at H, and is fitted into the flask by means of a stopper passed over the tube, A. When I and H are closed, and D is open, the pressure existing in the flask is exerted through A and C upon the upper surface of the liquid in the funnel; and on opening I, the same pressure being applied to its lower surface also, the liquid flows down through B, under a pressure dependent only on its specific gravity,

Fig. 1

Fig. 2
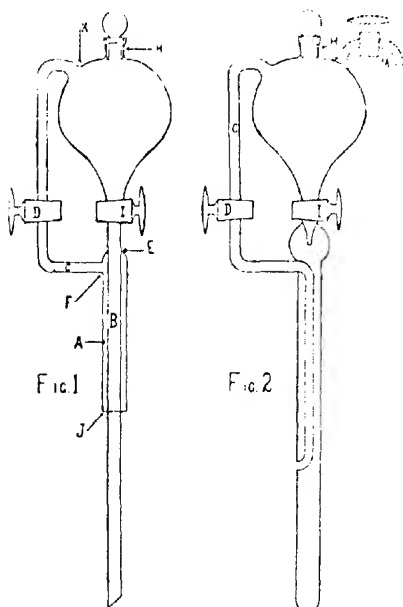
the height of its column, and the capillarity of the tube, B, which last may be neglected. The speed of delivery may be regulated by the tap, and a continuous or intermittent flow of liquid is possible so long as a single drop remains in the funnel. By closing D and I, and removing the stopper, fresh liquid may be introduced into the funnel.

Fig. 2 is a modification of Fig. 1, fitted with a Walter's dropping device, and the side, M, is useful when it is required to replace air in the apparatus with some other gas, or when it is undesirable to discontinue distillation *in vacuo* after refilling the funnel, in which case the funnel is exhausted through M, while D, I, and H are closed.

A cheaper form of the apparatus may be obtained, suitable for cases in which the reagents employed do not attack rubber, this latter being employed for making joints, etc.   W. H .S.

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REVIEW.

Food Inspection and Analysis for the Use of Public Analysts, Health Officers, Sanitary Chemists, and Food Economists. By Albert E. Leach, S.B. (New York: Wiley and Sons. London: Chapman and Hall. Price 31s. 6d.)

The scope of this work is wider than that of many of the books on food analysis published in this country, embracing other matters relating to the control of the food-supply in the United States of America. The book seems well adapted to meet the wants of those for whom chiefly it has been written. It is copiously supplied with references, especially as regards American publications, and also German; but as regards British work and publications, the references are certainly less complete.

In the author's country the working of the Food Acts is in some respects in advance of what, so far. has obtained here. Many of the States have in local laws adopted standards for milk and other articles, while Congress in 1903 empowered the Secretary for Agriculture to draw up from time to time schedules giving limits and standards for many articles of food. American writers are apt to assume that we are in like position, and hence the author speaks of British standards for vinegar and other articles, which at present do not exist.

In the preliminary chapters the duties of the Food Inspector and of the Public or Official Analyst are considered, also the fitting and equipment of the food laboratory, followed by a general classification of foods. The system of inspector's lockers, described on p. 7, may be suggestive to our home authorities.

Under the fitting of the laboratory a formula is given for the aniline black staining of laboratory tables, where the aniline solution is too strong for use. Sixty-five grams of water probably means 615 grams, as in the second solution (pp. 13 and 14).

The description of general analytical methods is fairly complete, but those for the estimation of arsenic might have been written before the arsenic scare here in 1900. The great advances then made in the application of the Marsh test are ignored, and the mirror test method is ascribed to Sanger in 1890, though he used for comparison test solutions of arsenic, 0·01 mgm. As in 1 c.c. (or 1 of As in 100,000 of solution). In the modern methods, 1, 2, 3, etc., c.c. of such a solution would give mirrors so dense as to be indistinguishable, unless only a small fraction of the arsenic was deposited in the mirror. Tests capable of detecting $\frac{1}{500}$ or even $\frac{1}{5000}$ grain of As per gallon must be some hundreds of times more delicate than the method described by the author.

In subsequent chapters no mention is made of the possible presence of arsenic in

malt derived from the fuel used in the malt-kilns. The presence of arsenic in vinegar is referred to, but not in other organic acids, nor in glycerine.

A very full account is given of milk and milk products. Obviously the minimum water in milk, given as 89·32 per cent., is a misprint for a lower number. One page is devoted to the "so-called" Adams' method, quoted without reference, while five pages are allotted to the Wollny Milk Fat Refractometer. This surely cannot indicate their relative importance.

In the estimation of milk-sugar, the Laurent instrument is referred to almost equally with the Soleil-Ventzke, but in the chapter on sugar the latter only is described in its various forms. In this chapter an error in the conversion table is noticeable which I find in other American books. 1° angular rotation is not equal to 0·7511° Wild's (sugar scale), but to ten times as much—7·511°.

Butter is relegated mainly to the chapter on edible oils and fats. While Hehner and Angell's names are given in the list of references at the end of the chapter, only ten lines are given at the beginning of the chapter to their pioneer work. The author speaks of the Reichert-Meissl number as "conclusive." Unfortunately extended experience does not show any one test as being quite conclusive.

Phytosterol and cholesterol are referred to and described, but no mention is made of the acetate method for the identification of phytosterol, nor is any reference made to the possible effect of the feeding of the animals on the milk and other products obtained from them.

The chapters on flesh foods and eggs give much information useful to meat and market inspectors. The detection of preservatives in meats, fish, etc., is indicated, also the distinctive characters of horseflesh, but nothing is said about the vexed question of the influence of tuberculosis or other germ diseases on the wholesomeness of the milk and products from animals so infected.

There are interesting chapters on cereals, vegetables, and fruits; on tea, coffee, and cocoa, and on spices. These are freely illustrated both in the text and in numerous plates at the end of the book. Some of the illustrations are wanting in clearness, but they indicate what each analyst should do for himself—prepare his own slides of pure materials and mixtures for comparison, without relying too much on any book illustrations.

Chapters on alcoholic beverages, vinegar, food preservatives, and tinned and canned foods, are also included. On p. 530 the specific gravity of a de-alcoholized liquor is given as 0·9872. If this is compared with water = 1, there is obviously some mistake. Probably the chapter on alcoholic liquids was written before so much attention was drawn to the subject by prosecutions for selling impure spirits, and this may explain why only the Rose method for the detection and estimation of the higher alcohols is given in the text.

On the whole, the book may be recommended as giving a good account of the experience and practice of American laboratories in the analysis and examination of food.   T. F.

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The monthly meeting of the Society was held on Thursday evening, June 14, in the chemical Society's Rooms, Burlington House. The President, Mr. E. J. Bevan, occupied the chair.

The minutes of the previous meeting were read and confirmed.

Certificates of proposal for election to membership in favour of Messrs. W Dickson and G. W. Monier-Williams, B.A., Ph.D., were read for the second time.

Messrs. H. G. Harrison, M.A., E. Miller, and F. W. Passmore, Ph.D., were elected members of the Society.

The following papers were read: "An Examination of the Methods of Milk Analysis used at the Government Laboratory in Connection with Samples of Milk referred under the Sale of Food and Drugs Acts," by H. Droop Richmond and E. H. Miller; "On the Examination of Linseed, Olive, and other Oils," by R. T. Thomson and H. Dunlop; and "On the Composition and Valuation of Oils for Gas-making Purposes," by Raymond Ross and J. P. Leather.

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A NEW METHOD OF ESTIMATING MOISTURE, WITH SPECIAL APPLICATION TO MOISTURE IN CORDITE AND OTHER SUBSTANCES CONTAINING VOLATILE MATTERS OTHER THAN WATER.

By P. V. DUPRÉ.

IN a paper on ammonium oxalate, which I had the honour to read before this Society in June last, a method of estimating moisture by means of calcium carbide was mentioned, and it was stated that experiments were in progress to apply the method more or less generally. These experiments having been now completed, I beg to lay the results before this Society.

A series of experiments was first undertaken to standardize the process. With this object ammonium oxalate was chosen, as affording the most convenient and

accurate method of weighing out a definite quantity of water, since the proportio[n] contains is accurately known (12·67 per cent.), and there is no tendency to loss evaporation during weighing.

Various weights of the salt, from 0·25 to 0·56 gram, equivalent to 0·03 0·07 gram of water, were taken, the quantity being weighed out in a tube of abo[ut] 1 cm. diameter and about 12 cms. long; the salt was then covered with a t[hin] layer of sand,* and calcium carbide filled in to a depth of about 5 cms. T[he] tube was then connected with a nitrometer containing a saturated solution common salt, and the apparatus adjusted to zero with the tube brought to a kno[wn] temperature by immersion in water. The tube was then immersed in a water-bath a temperature of 100° C. to a depth of 7 or 8 cms., and the heating continued un[til] no further evolution of gas could be observed. The tube was then brought back the original temperature and the volume of acetylene measured, the temperature a[nd] pressure being noted.

As the mean of ten experiments, in the last three of which the water w[as] weighed out direct, it was found that 1 c.c. of acetylene at N.T.P. was equivale[nt] to 0·001725 gram of water. The theoretical number would be 0·00162, but the temperature of boiling water the hydrate of lime formed retains a small p[ro]portion of water above the one molecule. As, however, the amount of hydr[ate] of lime formed is always proportional to the amount of acetylene evolved, th[e] relation between the amount of acetylene produced and the excess of water retain[ed] is always the same.

The following table gives the results obtained; it will be seen that the variat[ions] are small, and that the process is therefore of adequate accuracy:

Weight of Amount of Oxygen taken.	Weight of Water.	Amount found.	Error.
0·2430 gram	0·0308	0·0311	+0·0003
0·3003 ,,	0·0380	0·0378	-0·0002
0·3160 ,,	0·0401	0·0400	-0·0001
0·3235 ,,	0·0410	0·0413	+0·0003
0·4890 ,,	0·0620	0·0619	-0·0002
0·5020 ,,	0·0636	0·0634	-0·0002
0·5565 ,,	0·0705	0·0703	-0·0002
	0·0651	0·0649	-0·0002
	0·0298	0·0301	+0·0003
	0·0627	0·0625	+0·0002

The moisture in cordite was then estimated in exactly the same way, cordite ground as for analysis, being substituted for the oxalate, and from 1 to 2·5 gram[s] being taken. The total volatile matter in each sample was estimated at the sam[e] time by the official method. The following are the results:

* The sand is used to prevent contact between the oxalate and the calcium carbide, which mig[ht] cause loss of acetylene at ordinary temperatures. See paper on ammonium oxalate.

Nature of Sample.	Total Volatile Matter.	Moisture.	Acetone.
	Per Cent.	Per Cent.	Per Cent.
Cordite M.D.	0·41	0·29	0·12
Cordite M.D....	0·72	0·24	0·48
Cordite returned from India	0·36	0·23	0·13
First sample after softening with acetone for grinding...	5·39	0·60	4·79
Cordite Mk. 1, recent, size 20	0·27	0·11	0·16
Cordite Mk. 1, size 20, old ...	0·40	0·10	0·30
Cordite M.D., recent ...	1·04	0·34	0·70
Cordite M.D., old	0·80	0·44	0·36

In order to test the accuracy of these results the following experiments were made:

(a) Two samples were examined, each in duplicate, in order to see whether the results were concordant.

(b) A sample was taken and the moisture estimated as before; the experiment was then repeated with another portion, to which a drop of acetone had been added after weighing, to find out the effect, if any, of the presence of this body.

(c) A portion, previously dried, was weighed, exposed to moist air and again weighed, and the moisture so absorbed estimated as before.

The results were as follows:

	Sample I	Sample II.
First experiment	0·148 per cent.	0·114 per cent.
Second experiment	0·146 ,,	0·118 ,,

(b)		(c)	
Sample III.		Sample IV.	
Direct ... ... 0·416 per cent.		Water absorbed ... 0·345 per cent.	
+ acetone ... ... 0·419 ,,		Water found ... ... 0·344 ,,	

The method has also been applied to other substances, and found very useful in the case of a mixture containing a volatile constituent, such as naphthalene or camphor.

For instance, about 0·25 gram of naphthalene was taken and 0·0255 g. of water added ; the moisture estimated by the above method came to 0·026 gram.

Again, in an explosive containing such ingredients as ammonium oxalate magnesium sulphate, the total moisture can be rapidly estimated by this meth. whereas it takes a long time—several days in many cases—for these salts to lose their water of crystallization *in vacuo*, especially in such explosives as gelignite. The water present as moisture can readily be calculated when the proportion of the has been estimated.

Experiments are now in progress to find out whether the method can be appl to volatile liquids.

TIME IN MINUTES.
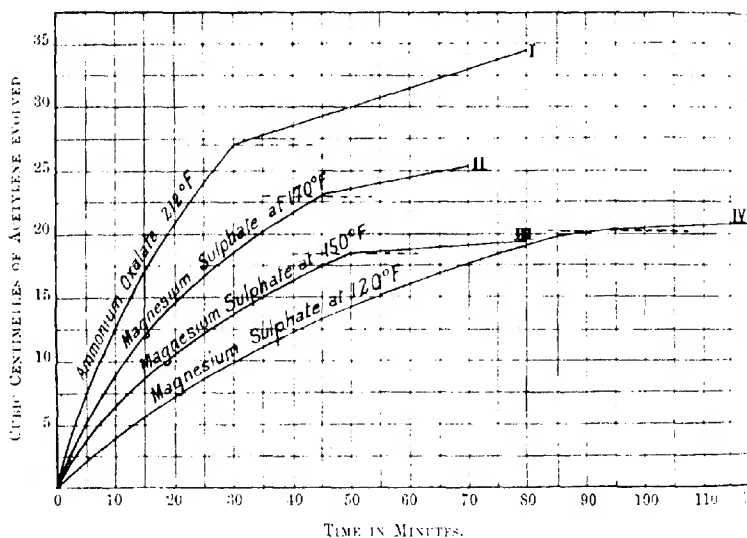
Experiments made in yet another direction with the view of distinguishing if possible, between water not in combination and combined water have yielded results which may prove to have some useful application. These experiments w carried out exactly as described in the paper on ammonium oxalate, except that the salt was taken in a moist condition, a known weight of water having been added, a the curve, representing the rate of loss of water at constant temperature, obtained The results show that the proportion of uncombined water can be separated v approximately from the combined water by means of a sharp change in the step ness of the curve, which occurs directly all the uncombined water has been driven.

It might be thought at first sight that a salt when so heated would lose add water only until all this had been driven off, and that it would only then begin to lose combined water. From the few experiments made, however, this does not appear be the case ; but, on the contrary, combined water commences to be lost at once.

loss continuing during the whole period taken for the uncombined water to the driven off. Also, this loss appears to take place at an average rate, during this period, of one-half the rate of loss of crystalline water after all uncombined water has gone.

The chart on p. 216 gives the results obtained. The black lines represent the observed volumes of acetylene, the observations being taken every five minutes and each marked by a circle. The dotted lines represent the heights at which the breaks in the curves should, theoretically, have occurred, calculated from the amounts of uncombined water taken and allowing for temperature and pressure, and also making the allowance above stated for the loss of crystalline water. The rate of loss taken is one-half that indicated by the curve after the break.

Weight of Uncombined Water taken.						Weight calculated from Curves.
CURVE I. 0·0080	..	...	...	.	.	0·0080
„ II. 0·0325	...	...	...	...	.	0·0323
„ III. 0·0275	...	...	...	.	...	0·0273
„ IV. 0·0325	...	...	..	...	...	0·0325

DISCUSSION.

THE PRESIDENT (Mr. Bevan) having invited discussion,

Mr. GUTTMANN said that the differentiation of the various volatile matters in cordite was not so unimportant as might at first be thought. Having regard to the important rôle that any volatilizable matter in a powder must play as far as ballistic results were concerned, it would be easily realized what an enormous difference there was between water and acetone. When it was remembered that ¼ per cent. of moisture might make an explosive absolutely unexplodable, while with ½ per cent. it might still be explosive, and having regard to the narrow margin allowed by official specifications and shooting tests, the great influence of even ½ per cent. of moisture would be readily understood. He remembered a paper by Mr. A. Marshall in the *Journal of the Society of Chemical Industry*, in which special means were described for condensing the nitro-glycerin, which would also be evaporated in the process. Mr. Dupré had not alluded to this, but presumably, at the temperature to which the cordite was heated, a good deal of nitro-glycerin would come off, and one wondered what happened to it. Was it included with the acetone? If so, these results would need bringing into order by some further work, and if Mr. Dupré could succeed in differentiating between the nitro-glycerin and the acetone either by applying Mr. Marshall's process or in some other way—he would make his method complete.

Mr. A. MARSHALL said that the first attempt to find a satisfactory method of determining the total volatile matter in cordite was made by a cousin of Mr. Dupré at Waltham Abbey. The details of the method were not altogether satisfactory, but further experiments which he (Mr. Marshall) had carried out at Waltham Abbey had resulted in its improvement. The method brought forward by Mr. Dupré advanced the question a stage further, as it enabled one to distinguish the water from the acetone or other volatile solvent used in manufacturing. Mr. Dupré's results brought out the interesting point that in cordite of uniform composition the amount of water was almost constant. Dr. Robertson, at Waltham Abbey, had by an entirely different method obtained similar results. The question arose whether that was really the

proportion of water in the cordite as used for firing, or whether it might not depend upon loss or gain of moisture from the atmosphere during the necessary process of grinding the cordite to powder. He had found that ground dried cordite exposed to the air absorbed just about the same amount of moisture in a few minutes, and as the preparation of the sample took at least several minutes, he thought that the constancy of the moisture might perhaps be accounted for in that way.

Mr. Dupré, in reply, said that no doubt a certain amount of nitro-glycerin was volatilized ; but he had heated some carefully dried cordite in the apparatus for ten or fifteen minutes without the evolution of any measurable amount of gas, and he had therefore concluded that whatever nitro-glycerin might be driven off was not decomposed in its passage through the carbide, but was condensed again probably at some part of the tube between the cordite and the nitrometer, and did not affect the volume of gas in the latter. The acetone distilled off would also be condensed, and a small allowance was made for it in the vapour tension. He might say that the method he had used was not intended in the least to supersede the official method of estimating the volatile matter, but it had struck him that it might be useful if the moisture and acetone could be separated. It was certainly possible that Mr. Marshall's explanation with regard to moisture might be correct, but in that case one would have to assume that 0·26 per cent. was the most that the cordite would ever take up, which from some of the results quoted does not appear to be the case.

✤ ✤ ✤ ✤ ✤

THE ESTIMATION OF FAT IN HOMOGENIZED MILK.

By H. DROOP RICHMOND, F.I.C.

(Read at the Meeting, May 2, 1906.)

HOMOGENIZED milk, or milk in which the fat is broken up into very small globules, not usually exceeding 0·001 mm. in diameter, is now an article of commerce. It is obtained by forcing milk under a pressure of from 200 to 400 atmospheres through very small openings ; there are several machines made for this purpose, differing from each other chiefly in the method of formation of the small openings. The cream in homogenized milk no longer rises freely, but remains to a very great extent distributed throughout the whole volume.

The process is chiefly applied to sterilized milk, which is often required to stand for a long time before being used, and from which it is an undesirable thing for the cream to separate ; but milk which has to stand—*e.g.*, on refreshment-bar counters— is also sometimes homogenized. It is therefore quite possible that some of the samples of milk taken under the Sale of Food and Drugs Act may be homogenized. As it appeared more than probable that the estimation of fat, especially by dry extraction processes, would be rendered more difficult by the fine state of division of the fat, I have made a few comparative experiments by different methods.

The methods chosen were those in common use by public analysts, together with the Kieselguhr method. In the Gottlieb and Werner-Schmid methods the

original plan of taking an aliquot portion was not followed, but the whole of the fat was dissolved out by repeated extraction. The Adams method was carried out by extracting a blank coil into a flask tared against the flask in which the fat was weighed. In the other methods the flask was, after weighing, washed out with petroleum ether, and weighed again with any residue of substance not soluble in petroleum ether. Very slight residues were almost always obtained, but so small, if due care had been employed, that the percentage of fat was barely affected. The following are the results:

Gottlieb.	Kieselguhr.	Werner-Schmid.	Adams.	Gerber.
3·79	3·80	3·81	3·58	3·78
3·70	3·70	3·74	3·52	3·70
3·66	3·66	3·67	3·53	3·70
3·46	3·46	3·45	3·32	3·47
3·86	3·87	3·88	3·66	3·89
3·93	3·94	3·98	3·81	3·95

It is seen that though the Werner-Schmid method has a tendency to be a trifle higher than the others, the first three methods are in almost perfect agreement, while the Adams method is always low. The Gerber method also gives good results with homogenized milk.

Microscopic examination shows that the fibres of the paper used for the Adams coils are very many times larger than the fat globules, while the diatoms of Kieselguhr have openings which are much smaller. Though the Adams coil provides sufficient surface to insure that the thickness of the film of milk solids is of the some order as the size of the fat globules in ordinary milk, and thereby exposes them to the solvent action of ether, it fails to do so when homogenized milk is extracted. The film is of sufficient thickness for some of the fat globules in homogenized milk to be completely surrounded with a layer of solids insoluble in ether. With kieselguhr there is a much larger surface, and the layer of milk solids is not thick enough to completely surround the globules.

The advent of homogenized milk renders it necessary to remove the Adams method from the position it has so long occupied as a standard method. In my laboratory it has for some time been discarded in favour of the Gottlieb method, which for ease and accuracy appears to be the best method we have, and I have little doubt that it will be in the future almost universally used.

✢ ✢ ✢ ✢ ✢

THE ANALYSIS OF DRIED MILK.

By H. DROOP RICHMOND, F.I.C.

MILK which has been evaporated to dryness is sold as dried milk or milk-powder. The methods of drying milk vary. The milk in one process is passed over polished steel rollers heated to a temperature above that of boiling water, and the film from which most of the water has been evaporated is taken off by knives set in a suitable position; in another process the milk is condensed in a vacuum pan to one-third or

one fourth of its bulk, and is then dried in a vacuum chamber in thin layers; in a third process the milk is, after a preliminary concentration, dried on hot rollers *cacao;* and there are other methods which have not come into extensive use.

The analysis of these milks requires a few slight modifications of the methods used for ordinary milk. The sample should be ground and well mixed to secure uniformity. *Moisture* is estimated by drying about 1 gram in the water-bath.

Fat cannot be estimated by direct extraction, as the results are always low. The Werner-Schmid method is suitable. If there is no sugar except milk-sugar, the fat after drying, should be dissolved in petroleum ether, and any residue weighed and subtracted from the total weight. In the presence of much of any other sugar, it is preferable to mix the ethereal solution with an equal bulk of petroleum ether, and shake out with water rendered slightly alkaline with ammonia before the solution is evaporated.

Milk-sugar may be easily and quickly estimated polarimetrically; 10 grams of milk-powder are ground up in a mortar with sufficient hot water to make it into a paste, which is gradually thinned with hot water, and the solution made up to 100 c.c.; a little ammonia may be added if the milk-powder does not all go into solution. Unless this procedure is followed, incomplete extraction of the sugar may result. The usual method is then followed.

Cane-sugar may be conveniently estimated by the method described by Harrison (ANALYST, xxx., 123).

Proteids are calculated from the total nitrogen by Kjeldahl's method by the factor 6·87.

Ash, Lime, and Phosphoric Acid as usual.

Acidity is estimated by grinding up about 1 to 2 grams with hot water, and titrating with $\frac{N}{10}$ alkali, using phenolphthalein as indicator.

The table below gives the analysis of seven samples:

TABLE I.—COMPOSITION OF DRIED MILK.

	1	2	3	4	5	6	7
Moisture	6·39	4·92	3·30	3·55	4·74	5·15	6·05
Fat	27·35	27·98	23·97	2·55	29·16	19·90	27·00
Milk-sugar	31·42	34·16	37·32	45·60	32·24	34·96	32·85
Cane-sugar	—	1·25	1·53	2·80	—	—	2·50
Proteids	27·48	24·59	26·38	35·45	26·66	31·10	23·84
Ash	6·00	6·24	6·19	7·89	5·63	7·11	6·44
Total	98·61	99·14	98·69	97·84	98·43	98·22	96·73
Water of hydration ...	1·65	1·80	1·96	2·40	1·70	1·84	1·73
Total	100·29	100·94	100·65	100·24	100·13	100·06	98·46
Change of temperature on mixing with water ...	−0·2°	±0·0°	−0·2°	−0·4°	−0·2°	..	−0·3°

It is noticed that none of the analyses add up to 100 per cent., but are considerably low; the milk-sugar has been calculated as anhydrous sugar, and here, I think, is the reason for the deficiency.

On shaking the solid residue obtained by drying milk on the water-bath, in which the milk-sugar certainly exists as anhydrous sugar, with water a rise of temperature always takes place; anhydrous milk-sugar mixed with water always causes a rise of temperature, whilst hydrated milk-sugar causes a fall of 0·55° if more than can be at once dissolved is added. The milk-powders examined, with one exception (No. 2), all caused a fall of temperature, and it is seen that the addition of the water of hydration to the total gives figures which are but slightly in excess of 100 per cent.; both the change of temperature and the slight excess over 100 per cent. indicate that the bulk of the milk-sugar, though not all, exists as hydrated sugar. Sample No. 2 differed in appearance from the others, being a heavy powder, instead of being light and flaky, and had doubtless been more dried, and probably contains a considerable proportion of anhydrous sugar; it is noticed that the addition of the water of hydration would make the total nearly 101 per cent. Sample No. 7 gives a low total, which I believe is accounted for by the presence of invert sugar.

It will be noticed that samples 2, 3, 4 and 7 contain small quantities of cane-sugar; this in sample 2 was admittedly added in the form of saccharate of lime, and was certainly so added, judging from the analytical figures, in No. 7. This is used to render the dried milk more soluble, and additions of sodium phosphate and other alkaline substances are made with the same object.

In Table II. the composition of the original milks, on the assumption that they contain 9·0 per cent. of solids-not-fat, are given.

TABLE II.—COMPOSITION OF ORIGINAL MILKS.

				1	2	3	4	5	6	7
Fat	...	...	...	3·79	3·88	3·09	0·26	1·07	2·45	3·65
Milk-sugar	...	...	...	4·36	4·73	4·81	4·62	4·50	4·30	4·68
Proteids	...	...	...	3·81	3·41	3·40	3·58	3·71	3·82	3·40
Ash	...	...	...	0·83	0·87	0·80	0·80	0·79	0·87	0·92
CaO	...	...	...	0·19	0·21	0·17	0·17	0·17	0·19	0·27
P O	...	...	...	0·23	0·24	0·23	0·23	0·23	0·29	0·24
Acidity	...	...	...	8·4	13·2	16·8	16·5	19·6	—	11·4

From this table it is seen that No. 4 is made from separated milk, and No. 6 from milk deprived of a portion of its cream. The milk used to prepare No. 3 is only just above the Government standard. The normal percentages of lime and phosphoric anhydride in milk are 0·17 per cent. and 0·23 per cent. respectively, but vary somewhat with the proteids, and the normal acidity is not far from 20°. From a consideration of the results, it would appear that Nos. 2 and 7 have received an addition of saccharate of lime; and No. 6 has received an addition of a phosphate. Nos. 3 and 4 contain cane-sugar, but there is no evidence of the addition of saccharate of

lime. No. 1 has probably received an addition of sodium carbonate, as the lime is not high enough, considering the high proteids, to indicate an addition of that substance; and No. 5 appears to have received no addition whatever.

DISCUSSION.

The PRESIDENT (Mr. Bevan), in inviting discussion, said that he could not quite understand how it was that, in the case of homogenized milk, the Adams process gave low results as compared with the Werner-Schmid and other methods. He should have thought that the breaking-up of the fat globules would have caused them to be more readily soluble. He should be interested to hear by what process the samples of dried milk referred to were made.

Mr. W. PARTRIDGE asked whether any unusual difficulty had been found in extracting the fat with ether in the case of homogenized milk. He had had occasion to examine some samples of condensed homogenized milk in which the degree homogenization was stated to be very high, and, using the Werner-Schmid process, his results were similar to those of a Norwegian analyst who had examined the same milks; but a London analyst who had also examined them, by Bell's process, had obtained results which were regularly 1 per cent. lower.

Mr. HEHNER said that he had made some time ago a few comparative experiments with regard to fat extraction in the case of dried milk prepared by the Hatmaker process, and had found in every case that a larger proportion of fat was obtained by extracting the powder itself with ether than by any other means. When plaster of Paris and other like materials were used lower results were invariably obtained. In the Hatmaker process, as in all others, alkali was added in the form of sodium carbonate, which would account for the somewhat high ash. He wondered why Mr. Richmond was so anxious that his analyses should add up to 100, seeing that there must necessarily be a number of undetermined constituents—for instance there would be about $\frac{1}{5}$ per cent. of citric acid in the milk, which, of course, would represent about $\frac{2}{5}$ per cent. in the dried product. He thought that the reason why, in the case of homogenized milk, the fat was not well extracted from paper was not quite satisfactorily explained by the photographs shown. When milk was mixed with an absorbent it evaporated, and the fat remained more or less adhering to the surface presented to it. It could not surely make much difference whether the absorbent was in small or large particles. The question must be whether the surface on which the fat was, so to speak, plastered was large enough to subdivide it completely, and he could not see why the surface presented by one material should be less favourable than that presented by another.

Mr. M. WYNTER BLYTH said that, from some experiments which he had made with certain foods for infants, he could confirm what Mr. Richmond had said as to the difficulty of extracting the whole of the fat by the Adams process. In one case he could only extract about 2 per cent. of fat, whereas a modification of the Werner-Schmid method, which he had used on Mr. Richmond's suggestion, yielded 5½ per cent. of fat. The low results given by the Adams process in such cases were explicable by the fact that, especially with malted foods, a dry mass of sugar was

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1906.

...ed which was very difficult to deal with. In the case, however, of milk in ...ch the fat globules had been broken up, he quite agreed with Mr. Hehner that ...e reason why the fat could not all be got out was difficult to understand.

Dr. LEATHER inquired how long the extraction with ether was carried on.

Mr. E. R. BOLTON asked whether the fat extraction was carried out in a Soxhlet apparatus or in one of those extractors in which the solvent dripped down and ...led straight through. He had found that in the case of oil cakes all the fat was ...acted much more quickly in such an extractor than in the Soxhlet apparatus.

Mr. WYNTER BLYTH said that in his case an ordinary Soxhlet apparatus was ...ed, and the extraction carried on for five hours.

Mr. RICHMOND, in reply, said that the milk-powders referred to were obtained by ...various processes described in the paper, but he did not know in all cases which ...cess had been used. Some of the samples were very finely ground, and had been ...ed to a greater extent, and probably contained a larger amount of anhydrous milk-...ar. It seemed to him that the photographs went a long way towards explaining ...lowness of the Adams results. It must be borne in mind that the photographs ...ot reproduced) were on different scales. Had they been on the same scale the ...ormous difference in the total surfaces exposed to the milk would have been ...ore apparent. In the case of kieselguhr the layer was of the same order of ...ickness as the fat globules, and consequently they were all exposed to the action ...f the ether. Probably, also, the grinding-up of the milk and kieselguhr had some ...fect. In the determinations by the Adams method extraction was carried on for ...t least five hours in a Soxhlet apparatus. In some cases extraction was carried ...t for so long as sixteen hours, but the full proportion of fat was still not obtained. ...had not found any difficulty with the Werner-Schmid process. He never made ...ore than four extractions, and at the fourth there was generally practically no fat ...t to take out. He had compared various methods of extracting, and had found ...ur extractions at the outside to be sufficient. This applied also to homogenized ...densed milk.

Mr. PARTRIDGE asked how much ether Mr. Richmond used for each extraction. ...e himself used about 15 or 20 c.c.

Mr. RICHMOND said that he used perhaps a little more, but not very much. In ...e case of homogenized milk he thought that the Gottlieb method had advantages ...er the Werner-Schmid. It took much less trouble, and the fat came out more ...anly and easily. With regard to the addition of alkali, he thought that sodium ...osphate was used quite as often as sodium carbonate.

Mr. HEHNER said that he had been consulted as regards the manufacture of ...ed milk both on the Continent and in America, and had never known any alkali ...t sodium carbonate to be used.

Mr. RICHMOND said that he knew that sodium phosphate had been used in ...land. With regard to the milk-sugar, having obtained distinct evidence from ...e change in temperature on mixing with water that there was some water of ...dration, he thought it only right to include this. He did not, of course, suggest ...at these analyses ought necessarily to add up exactly to 100. As Mr. Hehner ...d mentioned, there was citric acid present, which, however, was partly compen-

sated for by the fact that a portion of the phosphoric acid was inclu[...] both in the casein and in the ash. Analyses of dried milk should, however, [...] be $1\frac{1}{2}$ to $2\frac{1}{2}$ per cent. low.

Mr. FAIRLEY asked what, if the Adams process failed when the milk was spr[...] over a certain surface, was to prevent its being spread over a larger surface [...] dilution if necessary, and whether, in the Werner-Schmid determinations, [...] attempt had been made to find out whether any fixed residue was contained in [...] fat, because, after all, these discrepancies were minute, and a very small amount [...] impalpable mineral matter in the fat might make all the difference.

Mr. RICHMOND said that there was really nothing to prevent the milk be[...] spread over a larger surface. The fat in the Werner-Schmid determinations w[...] tested to see if it contained anything insoluble in petroleum ether, but was not ign[...] to see if there was any non-volatile matter.

Note.--In the *Journal of Analytical Chemistry*, vol. iv., part i., I stated : "Fr[...] the data given by Adams (ANALYST, x., 46), I calculate that on paper the thickne[...] the film of milk solids is less than 0·0002 inch, and from my own measurement[...] kieselguhr, I conclude that the film dried up on this medium is about 0·00[...] inch. . . ."] H. D. R.

✤ ✤ ✤ ✤ ✤

NOTE ON A RECENT PAPER BY R. STEINEGGER ON THE "ALDEHYDE FIGURE" OF MILK.

By H. DROOP RICHMOND, F.I.C., AND E. H. MILLER.

(Read at the Meeting, May 2, 1906.)

WE have been induced to refer to this paper by the fact that the method (ANAL. xxxi., 46) proposed is likely to be of considerable use.

The author first shows that formalin added to milk hinders and finally prev[...] curdling by rennet. Next he discusses the increase of acidity on the additio[...] formalin pointed out by Hanne and Hesse, and shows that the acidity increases w[...] the amount of formalin used and attains a maximum when about 5 per cent. (at [...] 1·8 per cent. of formaldehyde) is added, whether the addition is made all at [...] or in successive amounts.

He then gives the variations in the milk of *single cows*, and it is not pointed [...] in the abstract that the maxima and minima given are in the milk of single co[...] Next he shows that the increase of acidity is not due to the action of a ferm[...] causing oxidation to formic acid, as had been suggested by Hesse, and that it rem[...] constant whether rennet is added to the milk or not. In addition to giving fig[...] that show that the aldehyde figure is proportional to the total nitrogen in the m[...] and that the total nitrogen (and therefore the percentage of proteids) can be calcula[...] from the aldehyde figure, he gives some experiments with tyrosine and leuc[...] which show that the acidity is produced by the conversion of the amino groups [...] methylene-amino groups by condensation, with the consequent conversion o[...] amphoteric nature of the amino-acid into an acid one.

We think this paper important because—

1. The method appears to give an approximate estimation of the amino-nitrogen of the proteids.

2. It gives an indirect but very easy method for proteid estimation.

3. It adds another figure to those which can be easily determined in milk analysis, and thus will yield corroborative evidence.

Our first experiments were made with a view to see if we could obtain definite evidence of the combination with the amino-groups, and experimented with whey produced by the action of rennet and acid respectively.

Our results were :

	Treated with Benzene-diazonium Chloride	Dissolved and combined with β naphthol.
Acid whey	Dark red colour	Bright yellow precipitate
Acid whey + CH₂O	Dark yellow colour	No reaction
Rennet whey ...	Bright red colour	Light yellow colour
Rennet whey + CH₂O	Light yellow colour	No reaction

In each case the wheys effervesced in the cold on treatment with nitrous acid, whilst after treatment with formaldehyde there was no gas given off in the cold. The amount of gas given off from the rennet whey corresponded to 0·013 per cent. of amino-nitrogen, while the increase of acidity corresponded to about 0·01 per cent. of amino-nitrogen on the assumption that each molecule of NH corresponded to one equivalent of acidity. These results show the presence of both aromatic and fatty amino groups in milk which condense with formaldehyde.

We next experimented on a casein solution containing 0·2596 gram nitrogen by Kjeldahl per 100 c.c. ; this gave an aldehyde figure of 9·8 c.c. N soda per 100 c.c., and combined with 0·0394 gram CH₂O per 100 c.c., which is equivalent to 13·2 c.c. N alkali. Ten c.c. of this solution gave 0·1601 gram casein by precipitation with acetic acid, and 0·1608 gram after the addition of formaldehyde.

These results show that the " aldehyde figure " is not a complete measure of the amino-groups nor of the formaldehyde condensed.

Proteids certainly contain both amino and carboxyl groups, and when alkali is added (e.g., soda) the following reaction takes place :

$$R{}^{NH_2}_{COOH} + NaOH \rightleftharpoons R{}^{NH_2}_{COONa} + OH_2. \tag{1}.$$
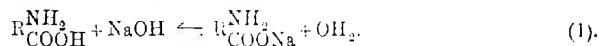
The point of neutrality to phenolphthalein is, on account of the presence of the basic NH₂ group, much nearer to the acid than to the sodium salt.

The action of formaldehyde is probably--

$$R{}^{NH_2}_{COOH} + CHOH \rightleftharpoons R{}^{N\ CH_2}_{COOH} + OH_2. \tag{2},$$
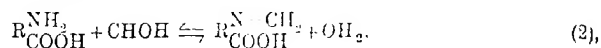
and the reaction in the presence of a large excess of formaldehyde is probably complete and very rapid.

The methylene-amino acid reacts with alkali thus :

$$R{}^{N=CH_2}_{COOH} + NaOH \rightleftharpoons R{}^{N=CH_2}_{COONa} + OH_2. \tag{3},$$
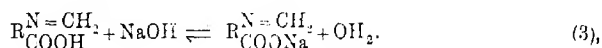
and the point of neutrality is probably very close to the salt on account of the feeble basicity of the methylene-amino group. The "aldehyde figure" measures the difference between the points of neutrality of the two reversible reactions (1) and

It is therefore by no means certain that all alkalies will give the same "aldehyde figure." We have measured in four samples of milk the "aldehyde figure" with soda and strontia respectively. The results are expressed as c.c. N alkali per litre.

ALDEHYDE FIGURES WITH

Soda.				Strontia.
1. 17·4	...	...	...	20·2
2. 20·1	...	...	...	21·6
3. 18·8	...	...	...	20·2
4. 21·8	...	...	...	22·6

The strontia "aldehyde figure" is always higher than the soda figure, and the mean ratio is 1·1.

We also find in mixed milk that soda gives a mean "aldehyde figure" of 18·4 while strontia yields 20·2, also in the ratio of 1·1.

Steinegger, who used the Soxhlet-Henkel method of determining acidity probably used soda as his alkali. We find that with soda 1 c.c. $\frac{N}{10}$ alkali corresponds to 0·0265 gram casein nitrogen, and 0·053 gram albumin nitrogen. Steinegger finds that on the average 1 c.c. $\frac{N}{10}$ alkali corresponds to 0·0303 gram of the nitrogen of milk (1 degree Soxhlet-Henkel = 2·5 c.c. $\frac{N}{10}$ alkali per 100 c.c. = 0·0758 gram N per 100 c.c.), whilst, taking the mean proportion of casein to albumin to be 7 : 1, we find 0·0298 gram using soda and 0·0271 gram using strontia.

As the titration is rather sharper with strontia than with soda, we prefer the use of the former solution.

The mean of 113 determinations gives 19·9 c.c. N strontia per litre of milk as the mean "aldehyde figure," with 22·6 c.c. as a maximum and 18·1 c.c. as a minimum. As showing the relative constancy in milk from a herd, we give the highest figures, the lowest figures, and a mean figure. All figures were on different dates:

			Aldehyde Figures.	Mean Solids-not-Fat.
Highest herd	...	...	21·0, 22·6, 22·0, 22·6	9·16
Mean herd	...	...	19·6, 20·2, 19·6, 19·6, 19·6	8·97
Lowest herd	...	...	18·1, 18·6, 18·1	8·61

We have also made a number of experiments on the change in the aldehyde figure when milk is acted on by micro-organisms, and on the amino groups in milk proteids. These will be discussed later.

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ANNIVERSARY DINNER OF THE SOCIETY OF PUBLIC ANALYSTS.

THE anniversary dinner of the Society took place on Wednesday evening, June 15, at the Trocadero Restaurant, under the chairmanship of the President, Mr. E. J. Bevan. Among the guests present were Sir Thomas Elliott, K.C.B., Secretary of the Board of Agriculture and Fisheries; Mr. John Lithiby, C.B., Assistant Secretary of

the Local Government Board ; Professor Percy F. Frankland, LL.D., F.R.S., President of the Institute of Chemistry ; Dr. Divers, F.R.S., President of the Society of Chemical Industry ; Mr. R. A. Robinson, President of the Pharmaceutical Society ; Mr. Montague Baird, President of the Institute of Brewing ; Dr. T. Cooksey, Deputy Analyst to the Government of New South Wales ; Sir William Ramsay, K.C.B., F.R.S. ; Professor J. Millar Thomson, LL.D., F.R.S. ; Professor W. A. Tilden, D.Sc., F.R.S. ; Dr. Buchanan ; Mr. F. W. Beck ; Mr. Richard B. Pilcher, Secretary of the Institute of Chemistry ; and Mr. Aubrey W. Bake.

The loyal toasts having been duly honoured, the following toasts were proposed : "Government Departments," by Sir William Ramsay, responded to by Sir Thomas Elliott and Mr. Lithiby ; " The Society of Public Analysts," by Professor J. Millar Thomson, responded to by the President ; " Kindred Societies," by Mr. Bertram Blount, responded to by Professor Frankland and Dr. Divers ; and " The Guests," by Mr. A. Gordon Salamon, responded to by Dr. Buchanan and Mr. R. A. Robinson. A choice selection of music, tastefully rendered by a select party of glee singers, added much to the enjoyment of the evening.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

Milk Substitute. R. Racine. *(Zeit. öffentl. Chem.,* 1906, xii., 167, 168.)—A preparation, sold to confectioners, under the name of artificial milk, has recently been examined by the author and found to consist essentially of sesame oil, sugar, and albumin. The results of the analysis were :

Total solids	...	...	...	...	85·90 per cent.
Ash	...	...	...	...	0·16 ,,
Oil (sesame)	...	...	...	.	47·10 ,,
Sugar (as invert sugar)		...	...	...	31·00 ,,
Albumin	...	...	...	...	1·51 ,,

The preparation was of a syrupy consistency, and, when mixed with water in any proportion, gave milky solutions from which the oil separated very slowly.

W. P. S.

Adulteration of Butter with Casein. R. Racine. *(Zeit. öffentl. Chem.,* 1906, xii., 169-170.)—A sample of butter was found by the author to have the following composition : Fat, 69·01 per cent. ; water, 24·73 per cent. ; ash, 0·77 per cent. ; casein, 5·49 per cent. This form of adulteration is readily detected owing to the large quantity of coagulum obtained on melting the sample. It will also be seen that an excessive quantity of water was contained in this butter. W. P. S.

The Detection of Bleached Flour in Wheat Flour. E. Fleurent. *(Comptes Rendus,* 1906, cxlii., 180 ; through *Journ. Pharm. Chim.,* 1906, xxiii., 499, 500.)—The

only processes of bleaching flour that have an industrial value are those in which nitrogen peroxide is used as the reagent. Pure oxygen or ozone does not affect the colour, and although ozonized air has a bleaching effect, it is only when it is simultaneously charged with nitrous products. Moreover, flours treated with ozone acquire a repulsive odour, which destroys their commercial value. The quantity of nitrous vapours in terms of nitrogen peroxide absorbed ranges from about 15 to 40 c.c. per kilogm. of flour. The nitrogen peroxide forms an addition compound with the fat the iodine value of which is correspondingly lowered. The action of ozone, however, causes an increase in the iodine value and the formation of volatile fatty acids. The fixation of the nitrogen peroxide by the fat affords a means of differentiating bleached from normal flour. Fifty grams of the sample are extracted with petroleum spirit (benzine), the extract evaporated at a low temperature, the residue of oil dissolved in 3 c.c. of amyl alcohol, and the solution shaken with 1 c.c. of a 1 per cent. alcoholic solution of potassium hydroxide. In the case of a normal flour the resulting soap solution is of the same pale yellow colour; but when the flour has been bleached the colour changes to reddish-orange, the depth of shade depending upon the amount of nitrogen peroxide that had been fixed by the fat. The test is capable of detecting the addition of 5 per cent. of bleached flour to ordinary flour. The bleaching process has no action upon the diastase or other enzymes of the flour, but the fat becomes acid more slowly than that which has not combined with nitrogen peroxide. It is in this sense only that the bleaching process can be said to have any preservative action upon the flour.   C. A. M

A Study of the Proteids of Beef-Flesh.   P. F. Trowbridge and H. S. Grindley.

(Journ. Amer. Chem. Soc., 1906, xxviii., 469-505).—The results of their previous work (ANALYST, 1905, 89) led the authors to the conclusion that much additional information regarding the proteids of flesh could be obtained by extracting the flesh successively with cold water, with a 10 per cent. ammonium sulphate solution, and finally with $\frac{N}{15}$ potassium hydroxide solution in the cold. An investigation on these lines was therefore carried out, together with a study of the acidity of the flesh, with the following results : The total acidity of aqueous extracts of flesh varies between comparatively wide limits, the minimum being 0·66 per cent., the maximum 1·07 per cent., and the average 0·85 per cent., calculated as lactic acid and expressed in terms of the fresh meat. Whilst the residues of flesh which are left after complete extraction with cold water are distinctly acid to litmus and to phenolphthalein, the insoluble proteids of flesh upon digestion with $\frac{N}{15}$ hydrochloric acid, at the ordinary temperature, combine with the latter, neutralizing its acid properties.

The analyses show that 13·56 per cent. of the total proteids existing in lean flesh is soluble in cold water. Of this, 90·04 per cent. is coagulable by heat from a neutral solution, 8·40 per cent. exists in the form of albumoses, and a very small quantity apparently as peptones. It is not at present supposed that the albumoses and peptones exist as such in the original flesh. During the coagulation of an aqueous extract of flesh there is an increase in the acidity of the same. Reduction of the acidity of the extract facilitates the coagulation of the proteids, the separation

of the coagulable proteids being more complete with one-fourth neutralization (to phenolphthalein) of the acidity of the extract than it is on further neutralization. The partial neutralization of such extracts causes the precipitation of some proteid matter at the ordinary temperature. There is no well-defined temperature at which different coagula of flesh extracts separate. The complete removal of the proteid coagulating at any definite temperature requires long application of heat, and the lower the temperature at which a coagulum is separated, the longer the time required to effect the separation.

Of the total proteid of a cold water extract of flesh, 11·71 per cent. is separated by neutralization, 36·65 per cent. is coagulable below 50° C., 39·99 between 51° and 75° C., and 11·71 between 76° and 85° C. The chemical composition of the different fractional coagula is remarkably constant, and, judging from the results of their hydrolysis, their chemical constitutions are quite similar.

Raw flesh which has been completely freed from proteids soluble in cold water contains two classes of proteid substances—those which are soluble in 10 per cent. ammonium sulphate solution and those which are insoluble. Of the total proteids of lean flesh about 16 per cent. are insoluble in cold water, but soluble in 10 per cent. ammonium sulphate solution. The latter solution extracts from flesh at least two individual proteids or groups of proteids which differ in physical properties, and to some extent in chemical composition.

The residue left after extracting raw flesh with cold water and 10 per cent. ammonium sulphate solution is almost entirely soluble in N potassium hydroxide solution, and has the same chemical composition even when separated from the solvent by different means and purified by widely different treatment.

W. P. S.

The Presence of Sodium Arsenate in Preserved Meat. A. Andouard.
(*Journ. Pharm. Chim.*, 1906, xxiii., 417, 418.)—Sodium nitrate has gradually replaced potassium nitrate as a means of giving to preserved pork the rosy colour of the fresh meat. In the author's opinion, it is less injurious than nitre, but he considers that the use of any alkaline nitrate for such purposes should be prohibited, both on account of their active medicinal properties and of the risk of poisoning from the use of impure salts. Several instances of such poisoning have come under his notice, and in three cases the supposed sodium nitrates used for colouring the flesh were found to contain sodium arsenate. C. A. M.

Determination of Fat in Cocoa. A. Kirschner. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, vol. 11, pp. 450, 451.)—The following manner of applying the Gottlieb process (ANALYST, 1898, 259) to the determination of fat in cocoa is described: A weighed quantity of about 1·5 grams of the cocoa and 20 c.c. of alcohol (50 per cent. by volume) are shaken together in a graduated cylinder. The latter should have a capacity of 75 or 100 c.c., be divided into divisions of 0·5 c.c., and be of such a diameter that the height between the 0 and 75 c.c. marks is not less than 30 cm.; 25 c.c. of ether are then introduced, and the mixture shaken for fifteen minutes, when 25 c.c. of petroleum spirit are added and mixed by carefully inverting the cylinder

a few times. Care must be taken not to form an emulsion. The cylinder is now set aside for one hour to allow the solvent to separate, 45 c.c. of the ethereal layer being then withdrawn, evaporated, and the residue of fat weighed. As the presence of the cocoa prevents the total volume of the solvent being read off, a blank experiment is made, in which the above-mentioned quantities are used, but the cocoa omitted, and the volume thus ascertained. To the total volume found in this manner is added the weight of fat obtained, 1 c.c. being added for each gram. The amount of fat in the cocoa is then found by a simple calculation. From the results given the process appears to be trustworthy.   W. P. S.

The Determination of Foreign Substances in Cocoa and Chocolate. F. Bordas and Touplain. (*Comptes Rendus*, 1906, xlii., 794; through *Journ. Pharm. Chim.*, 1906, xxiii., 502, 503.)—Foreign substances are usually searched for with the microscope in the insoluble residue left after extraction of the fat with ether and of the sugar with water. To simplify the process, the authors have devised a mechanical method of separating the different substances by treating the residue successively with mixtures of carbon tetrachloride and petroleum spirit (benzine), ranging in specific gravity from 1·340 to 1·600. Preliminary experiments have shown that the different substances that may be in the insoluble residue behave as follows on treatment with the different mixtures :

Specific Gravity.			Insoluble Residue of—			Behaviour.
1·340	...	...	Arachis cake	...	...	Sinks
1·435	...	...	,,	...	...	Floats
1·400	...	...	Cocoa germs	...	...	Sink
1·440	...	...	,,	...	...	Float
1·440	...	...	Pure cocoa	..	...	Sinks
1·500	...	...	,,	...	...	Floats
1·500	...	...	Husks	..	...	Sink
1·530	...	...	,,	...	...	Float
1·510	...	...	Potato starch	...	...	Sinks
1·525	...	...	,,	...	...	Floats
1·600	...	...	Mineral matter	...	...	Sinks

C. A. M.

A Reaction of Theobromine. G. Gérard. (*Journ. Pharm. Chim.*, 1906, xxiii., 476, 477.)—A small quantity (0·05 gram) of the alkaloid is mixed with 3 c.c. of water and 6 c.c. of sodium hydroxide solution (*lessive des savonniers*), and the tube allowed to stand until the liquid becomes clear, after which 1 c.c. of ammonium hydroxide and 10 c.c. of a 10 per cent. solution of silver nitrate are introduced. The mixture on shaking forms a colourless transparent mass, which becomes fluid at 60° C., and sets to a *transparent* jelly when cooled again. If the heating be done too rapidly, too concentrated solutions of the alkaloid yield opaque jellies. In the author's opinion, the reaction is probably due to the formation of a silver precipitate of theobromine in a gelatinous state similar to that of precipitated silica. Caffeine does not give the reaction. The test is very sensitive, and it is possible to obtain

evident solidification with 0·01 gram of theobromine in 10 c.c. of liquid. When once formed, the jelly can be kept for several weeks without undergoing any alteration.

C. A. M.

Detection of Sugar in Mace. E. Spaeth. (*Zeit. Untersuch. Nahr. Genussm.,* 1906, vol. 11, pp. 447-450.)—Notwithstanding the fact that mace contains naturally a small quantity of sugars (*cf.* ANALYST, 1905, 207), the presence of added sugar may be detected by the following test, described by the author some years ago (1896): Ten grams of the sample, previously freed from fat by means of petroleum spirit, are shaken with chloroform and allowed to settle. After decanting the greater part of the latter, the last few c.c., together with the sediment, are evaporated on the water-bath, and the residue dissolved in a little warm water. The solution is clarified by the addition of lead acetate and aluminium hydroxide (the latter alone is usually sufficient), diluted to 50 c.c. with water, filtered, and the filtrate examined by the polarimeter. When thus treated pure samples of mace yield no polarizing substances, and, consequently, the presence of added sugar is readily detected. W. P. S.

The Ash of Pepper and Cinnamon. H. Lührig and R. Thamm. (*Zeit. Untersuch. Nahr. Genussm.,* 1906, xi., 129-134.)—The following results were obtained on the analysis of specimens of Malabar, Tellicherri, and Singapore peppercorns, 9 samples in all being examined. The figures represent percentages on the sand-free dry substance. The amount of sand present varied from 0·010 to 0·265 per cent.:

		Ash.			Alkalinity of Ash: c.c. N Acid per 100 Grams of Pepper.		
		Total.	Water-soluble.	Water-insoluble.	Total.	Water-soluble.	Water-insoluble.
Average	...	5·02	3·19	1·83	52·4	26·2	26·1
Highest	...	5·60	3·57	3·14	54·9	28·6	38·3
Lowest	...	4·67	2·46	1·49	49·1	15·7	20·5

Eight samples of Ceylon cinnamon gave the following results:

Average	...	5·28	1·56	4·72	92·2	14·7	77·5
Highest	...	5·96	1·84	4·32	101·5	18·1	88·6
Lowest	...	4·30	1·26	3·00	72·9	11·0	70·5

Two samples of cassia bark—a common adulterant of cinnamon—gave results as under:

1.	2·36	0·90	1·46	34·5	5·95	28·6
2.	2·37	0·96	1·41	35·6	6·14	29·1

For the determination of the soluble alkalinity of the ash, the latter, after being weighed, was washed into a 100 c.c. flask with about 50 c.c. of water, boiled for ten minutes, then cooled and made up to the mark. The solution was filtered, and 50 c.c. of the filtrate boiled with the addition of an excess of $\frac{1}{4}$ N acid. The excess of the latter was then titrated back with $\frac{1}{4}$ N alkali solution. The whole of the contents of the 100 c.c. flask were now brought on to the filter, washed with a large volume of boiling water, and the insoluble ash determined as usual. The samples of cinnamon contained very little sand—viz., from 0·02 to 0·08 per cent. W. P. S.

The Detection of Soap-Wort in Mineral Waters. J. Vamvakas. (*Ann.*
de Chim. anal., 1906, vol. 77, 161-163.)—A decoction of soap-wort root (*Saponaria*
officinalis) is a common addition to mineral waters, and various preparations con-
taining it are used to produce frothing when the bottle is opened. One of these
of English origin, examined by the author, was sold under the name of "Liqueur
Lautain." It was a brown liquid with an odour of banana, an acid reaction, and a
density of 1·140 at 15° C. It consisted, in the main, of an aqueous extract of soap-
wort root, and contained 1·6 per cent. of sugar. When diluted with water, boiled
cooled, and treated with a few drops of Nessler's reagent, it gave a bright yellow to
deep orange-coloured precipitate, which became greenish-gray after a few hours, and
finally leaden-gray. A similar reaction was obtained with decoctions of soap-wort
root and with mineral waters containing it. If the liquids were boiled after the
addition of the Nessler's reagent, a gray precipitate, changing immediately to blackish-
gray and greenish-gray, was formed. The addition of a few drops of nitric acid or
of a concentrated solution of tartaric acid prevented the formation of any precipitate
by the reagent. The following method of applying the test to lemonade and other
mineral waters is recommended: 100 c.c. of the liquid are boiled to expel the car-
bonic acid and the free ammonia in the water, diluted to the original volume
again, and treated with lead subacetate. The white precipitate is filtered off, sus-
pended in water, and decomposed with a current of hydrogen sulphide, abundant
frothing being produced if the original liquid contained soap-wort extract. The liquid
is now filtered, and the filtrate and washings boiled until quite free from hydrogen
sulphide, cooled, and divided into three parts. One of these is tested with Nessler's
reagent and allowed to stand, the second boiled with the reagent, and the third tested
with a few drops of a concentrated solution of tartaric acid in the hot as well as in
the cold solution. If the drink contained soap-wort, a yellow precipitate will be
obtained in the first case, a greenish or grayish-black precipitate in the second, and no
precipitate at all in the third. The reaction is not applicable to sparkling wines
or to beer. C. A. M.

The Acids occurring in Raspberry Juice. R. Kayser. (*Zeit. öffentl. Chem.*
1906, xii., 155, 156.)—The following organic acids were detected and their quantity
determined in (1) a sample of raspberry syrup, and (2) raspberry juice preserved with
alcohol. The figures express grams per 100 c.c. after allowing for the amounts of
sugar and alcohol respectively present:

	1.	2.
Tartaric acid	0·220	0·180
Citric acid	0·756	0·655
Malic acid (by difference)	0·220	0·300
Volatile acid (as acetic)	0·060	0·045

W. P. S.

Composition of Raspberry Juice. Hefelmann, P. Mauz and F. Muller.
(*Zeit. öffentl. Chem.*, 1906, xii., 141-155.)—The average results of the analyses of fifty
samples of 1905 raspberry juice were found to be as follows:

				Total Solids. Per Cent.	Ash. Per Cent.	Alkalinity of Ash. Cc. N A. sd.
Average	...	...	...	4·09	0·430	5·61
Maximum		...	...	4·94	0·505	6·90
Minimum	...	...	...	0·89	0·312	4·50

These results are in agreement with those found for other years.

W. P. S.

The Composition of Tamarind Pulp. O. Remeaud. (Journ. Pharm. Chim., 1906, xxiii., 424-429).—The following percentage results were obtained in the analysis of pulp prepared from the fruit by the author and of two commercial products:

	Dry Extract.	Water and Substances Volatile at 100° C.	Ash.	Substances Insoluble in Water.	Total Acids as Tartaric Acid.	Free Tartaric Acid.	Potassium Bitartrate.	Phosphoric Acid.	Other Acids as Tartaric Acid.	Cane Sugar.	Invert Sugar.	Pectin.
Prepared pulp ...	62·83	37·17	2·82	6·25	11·73	5·71	6·65	0·25	3·60	3·31	0·07	9·22
Commercial pulp, purified ...	73·04	26·96	3·26	7·08	15·34	7·03	7·31	0·37	3·38	31·28	0·46	
Commercial pulp, crude, without seeds	73·03	26·96	3·19	12·35	15·80	7·36	6·57	0·27	3·91	32·00		1·38

The prepared pulp differed from the commercial products in containing less total acids, somewhat less potassium bitartrate, and much more invert sugar. The fruit from which it was obtained contained 29·31 per cent. of pulp and 37·07 per cent. of seeds.

C. A. M.

Composition of Lemon Juice. H. Lührig. (Zeit. Untersuch. Nahr. Genussm., 1906, vol. 11, pp. 441-445).—The following results were obtained on the examination of ten samples of lemon juice pressed from the fruit in the author's laboratory, the figures expressing grams per 100 c.c. of the fresh juice, an allowance having been made for a quantity of alcohol added for preservative and clarifying purposes: Total solids, 10·181; citric acid (anhydrous), 7·586; ash, 0·3643; nitrogen, 0·059; invert sugar, 1·572; glycerol, 0·220; phosphoric acid, 0·0232; alkalinity of the ash, 4·99 c.c. N acid.

W. P. S.

The Detection of Camphene in Essential Oils. L. Balbiano. (Reale Accad. dei Lincei; through Journ. Pharm. Chim., 1906, xxiii., 397.)—Camphene combines with mercuric acetate to form a crystalline addition compound, $C_{10}H_{16}OHg(C_2H_3O_2)_2$, which is insoluble in water, alcohol, and ether, and can be decomposed by a current of hydrogen sulphide with liberation of the camphene. Pinene is oxidized by the reagent, but does not yield a crystalline derivative. In applying the test, the essential oil is mixed with its own volume of benzene, and shaken with a sufficient quantity of a 25 per cent. aqueous solution of mercuric

acetate (2 molecules of mercuric acetate to 1 molecule of camphene). The crystalline precipitate formed after thirty days' contact is readily purified owing to its insolubility in most neutral solvents, and the camphene can then be recovered by means of hydrogen sulphide. C. A. M.

The Lemon-scented Ironbark and its Essential Oil. R. T. Baker and H. G. Smith. (*Pharm. Journ.*, 1906, vol. 76, pp. 571, 572.) This small tree (*Eucalyptus staigeriana*) which is only at present found in Queensland, is a species with distinct characteristics and is not easily confounded with any other eucalyptus. The leaves examined by the authors yielded 2·481 per cent. of essential oil, having a light lemon colour and an odour of citral and geraniol. The rotation of the oil in a 100 mm. tube was −43·1 ; the specific gravity at 16° C. was 0·8708, and the refractive index at the same temperature 1·4871. The approximate composition of the oil was: Limonene, 60·00; geraniol, 12·72; geranyl acetate, 8·32; citral, 16·0; undetermined, 2·96 per cent. From the physical properties of the fractions obtained on distillation, it is seen that nearly the whole of the terpene present was laevo-limonene. W. P. S.

Peru Balsam Oil. Haensel. (*Haensel's Report*, 1906; through *Pharm. Journ.*, 1906, vol. 76, p. 612.) Genuine balsam contains about 30 per cent. of essential oil which is dark yellow in colour, has a slight dextro rotation, and a specific gravity of 1·083 at 25° C. The amount of cinnamein in this oil is 84·4 per cent.

W. P. S.

Determination of Camphor in Camphor Liniment. J. Lothian. (*Pharm. Journ.*, 1906, vol. 76, pp. 493, 494.)—Results of analyses are given showing that the camphor is completely volatilized from camphor liniment by heating a thin layer of the latter in a shallow, flat-bottomed basin for one hour on the water-bath. The size of the basin employed should be such that about 4 grams of the oil form a layer in it 1 mm. in depth. Under these conditions the olive oil itself does not gain in weight. W. P. S.

On a Reaction of Morphine. C. Reichard. (*Pharm. Centralh.*, 1906, xlvii., 247 ; through *Chem. Zeit.*, 1906, xxx. [*Rep.*], 142.)—The formaldehyde reaction for morphine is usually carried out in the presence of concentrated sulphuric acid ; the author finds it better to add a trace of stannous chloride instead of the acid. As modified thus, the reaction is a delicate test for either morphine or tin. A. G. L.

A New Reaction of Morphine. D. Radulescu. (*Bull. Soc. Sci. d. Bucarest*, 1905, 14, 602 ; through *Pharm. Journ.*, 1906, vol. 76, p. 501.)—The following colour reaction is stated to be peculiar to morphine : A filtered decoction of the substance to be examined, as free as possible from colour, is treated with a crystal of sodium nitrite and sufficient acid to liberate the nitrous acid. Before effervescence has ceased an excess of potassium hydroxide solution is added. In the presence of morphine a pale rose to ruby-red tint develops, according to the amount of morphine

present. The kind of acid employed is immaterial, and any alkali may be used. The red colour is not removed by shaking with immiscible solvents nor discharged by boiling the alkaline solution, but is decomposed by strong acids. It also decomposes in the presence of much alcohol. W. P. S.

On the Precipitation and Quantitative Determination of Alkaloids by means of Solutions of Potassium Bismuth Iodide. D. Jonesen. (Ph. pharm. Ges. Ber., 1906, 130; through Chem. Zeit., 1906, xxx. Rep., 156.) Thoms has shown that potassium bismuth iodide may be used, not only to detect organic bases, but also for the precipitation of certain alkaloids. The reagent is added to a sulphuric acid solution of the alkaloid, and the precipitate washed with dilute sulphuric acid. From the precipitate the alkaloid may be recovered by treatment with a mixture of sodium carbonate and hydrate (which treatment requires to be prolonged in some cases). In this way, from 1 gram each of quinine, caffeine, and antipyrin, 0·9405, 0·9516, and 0·9273 gram respectively was recovered, showing the precipitation with the potassium bismuth iodide reagent to be fairly complete.

A. G. L.

ORGANIC ANALYSIS.

The Determination of Methyl Alcohol in Formalin. O. Blank and H. Finkenbeiner. (Berichte, 1906, xxxix., 1326, 1327.) Methyl alcohol is an ordinary constituent of the commercial (40 per cent.) solutions of formaldehyde, an addition of 12 to 18 per cent. being made to prevent the liquid becoming permanently turbid when exposed to cold. The author bases a method for its determination on the amount of oxygen consumed when a weighed quantity of the formalin is oxidized by means of chromic acid and sulphuric acid—

$$H.COH + O_2 = CO_2 + H_2O$$
$$CH_3OH + 3O_2 = CO_2 + 2H_2O.$$
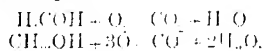
One gram of the sample is introduced into a mixture of 50 c.c. of chromic acid solution with 20 c.c. of strong sulphuric acid, and the whole allowed to stand for about twelve hours at the ordinary temperature, or about one to one and a half hours if the liquid be heated cautiously, care being taken not to let it evaporate below a third of its volume.

The liquid is then made up to a litre and 50 c.c. withdrawn, and, after the addition of a crystal of potassium iodide, titrated with a sodium thiosulphate solution. From the result the total amount of oxygen consumed can be calculated, and, the amount of formaldehyde in the original solution being known, the percentage of methyl alcohol can be obtained indirectly. In a test experiment described the result obtained was identical with the amount (7·65 per cent.) of methyl alcohol added to a 20 per cent. solution of formaldehyde. C. A. M.

New Method for the Determination of Acetone. S. J. M. Auld. (Journ. Soc. Chem. Ind., 1906, xxv., 100, 101.)—The acetone in wood spirit, crude acetone, etc., is converted into bromoform, the latter decomposed with alcoholic potash, and
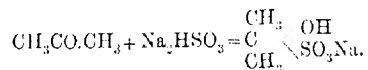
the residual potassium bromide titrated with silver nitrate solution, the hydrolysis being represented by the equation—

$$3CHBr_3 + 9KOH + C_2H_5OH = 3CO + C_2H_4 + 9KBr + 7H_2O.$$
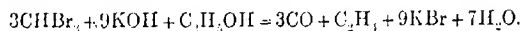
A quantity of the solution containing 0·1 to 0·2 gram of acetone is pipetted into a 500 c.c. round-bottom flask, diluted with a little water, and mixed with 20 to 30 c.c. of a 10 per cent. potash solution. The flask is attached to a long reflux condenser, and is fitted with a dropping funnel containing a solution of 200 grams of Br and 250 grams of KBr per litre. This solution is allowed to flow into the mixture until it has acquired a faint yellow tinge, the flask heated on the water-bath at about 70° C. for half an hour, and more bromine solution added drop by drop until the slight coloration is permanent, any excess being removed by boiling with a little more potash. The mixture is then distilled until the distillate is free from bromoform, water being added to the contents of the flask if necessary, and the condenser rinsed with a little alcohol. Distillate and washings are mixed with 50 c.c. of alcohol and sufficient solid caustic potash to make an approximately 10 per cent. solution, and the mixture heated on the water-bath under a reflux condenser until the bromoform is completely decomposed, which occupies about three-quarters of an hour. After evaporating to smaller bulk, if necessary, the liquid is cooled, neutralized with dilute nitric acid, diluted to 500 c.c., and an aliquot part titrated with $\frac{N}{10}$ silver nitrate, using K_2CrO_4 as indicator; 240 parts of bromine correspond to 58 parts of acetone. Pure bromine must be employed, as crude bromine frequently contains bromoform.

W. H. S.

The Determination of Acetone. A. Jolles. (*Berichte*, 1906, xxxix., 1304, 1307.)

The method is based upon the fact that acetone combines with sodium bisulphite (1 molecule : 1 molecule), forming the sodium salt of a sulphonic acid similar to that obtained with furfural (ANALYST, xxxi., 116)—

$$CH_3CO.CH_3 + Na_2HSO_3 = C\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\begin{matrix} OH \\ \\ SO_3Na. \end{matrix}$$

The standard bisulphite solution is added to the acetone solution in a quantity three or four times greater than the theoretical amount, and the excess is titrated with standard iodine solution after the mixture has been allowed to stand for not less than thirty hours. A blank determination with the sodium bisulphite solution should be made simultaneously to obtain the correction for any changes it may undergo during the experiment.

C. A. M.

Experiments made with Dettmarsch's Apparatus for Testing Oils. Richard Kissling. (*Chem. Zeit.*, 1906, xxx., 152.)

The author has made over 500 tests on the Dettmarsch apparatus (shown in the figure) for testing the lubricating power of oils. The apparatus consists essentially in two heavy fly-wheels, *a* and *b*, connected by a shaft revolving in a journal between them, to which the oil to be tested is fed from the reservoir (*h*, situated just under the right-hand bearing), where it is heated electrically. The fly-wheels are driven by the motor, *c*, and can

be instantaneously disconnected from the latter by releasing a spring, *t*. The method of working is to impart a certain measured velocity to the fly wheels, then to release the spring, and to measure the time taken for the revolution to stop entirely. From these data a "coefficient of friction" is calculated. Although the apparatus often gives results in good agreement with the viscosity determinations and the results
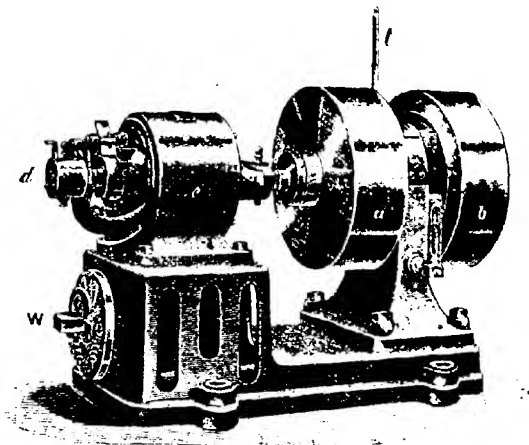
obtained in practice, the author has obtained so many totally inexplicable results with it (apparently attributed by him to the presence of an imperfection in the apparatus) that he condemns it entirely. He believes the only way to determine the lubricating power of an oil to be to test it *in situ* in the machine for which it is to be used.   A. G. L.

Preparation of Aldehyde-free Ethyl Alcohol for Oil and Fat Analyses.
F. L. Dunlap. (*Journ. Amer. Chem. Soc.*, 1906, xxviii., 395-398.)—Alcohol yielding a colourless potash solution may be obtained by adding to 1 litre in a glass-stoppered cylinder a solution of 1·5 grams of silver nitrate in 3 c.c. of water, mixing thoroughly, then pouring in slowly, and without shaking, a solution of 3 grams of potash in 10 to 15 c.c. alcohol. The finely-divided silver oxide precipitated gradually distributes itself through the alcohol, and after standing overnight completely settles, when the clear, supernatant liquid is filtered or siphoned off and distilled.
                                                                          W. H. S.

On the "Milkiness" of Paraffin Wax.   H. Mittler and R. Lichtenstern.
(*Chem. Rev. Fett. u. Harz-Ind.*, 1906, xiii., 101, 105.)—Transparent paraffin wax fetches a higher price than "milky" wax, and the greater value of the clear products is due to more than their better appearance. Neustadtl concluded that "milkiness" was caused by differences in the melting-points of the different constituents of the paraffin; but the authors contest this, and point out that transparent paraffins with

melting-points as far apart as 57˚ and 42˚ C. can be mixed together without rendering the product opaque, though in some instances a bluish shade may be produced. They attribute the "milkiness" to the presence of paraffin oil, and have isolated that oil from "milky" paraffin by extraction with a mixture of alcohol and ether, and have rendered transparent paraffins "spotted" or "milky" by adding oil in the proportion of 0·5 to 3 per cent. The addition of smaller quantities up to 0·3 per cent. has little or no effect upon the transparency.　　　　　　　　　C. A. M.

Constants of Carnaüba Wax. L. G. Radcliffe. (*Journ. Soc. Chem. I..,* 1906, xxv., 158.)—The following figures have been obtained with a sample of Cear. wax : Melting-point (in capillary tube), 84˚ C. ; acid value, 2·9 ; acid value determined by dissolving 3 grams in 120 c.c. of boiling amyl alcohol, 5 ; saponification value (5 grams dissolved in 60 c.c. amyl alcohol, and boiled for six hours with 50 c.c. alcoholic potash containing 60 grams of potash per litre), 88·3 ; ester value, 85·4 ; iodine value, 13·17. The bleached wax melted at 61˚, and had an acid value in amyl alcohol solution of 0·56.　　　　　　　　　W. H. S.

On the Proportions of Pentosan and Methylpentosan in Plant Products. **John Sebelien.** (*Chem. Zeit.,* 1906, xxx., 401.)—P. Sollied has continued the work done by the author and others to show that in the great majority of cases the amount of methylpentosan occurring in plants is considerably less than that of the pentosan also present. Sollied's results are given in the following table, Tollens and Ellett's method (*Ber.,* 1905, 492) having been used :

	Methylpentosan, Per Cent.	Pentosan, Per Cent.
Oak-wood, fifteen-year-old tree	2·26	19·06
Ditto, younger	2·31	18·60
Oak-bark, eighteen-year-old tree	2·08	14·21
Ditto, younger branches	2·54	12·95
Cedar-wood	2·90	12·36
Fir-wood	4·70	10·03
Beech-wood	2·68	23·59
Ash-wood	2·95	17·24
Hay	2·13	17·43
Fucus vesiculosus	3·16	6·32
Ascophyllum nodosum	3·47	8·46
Rye-bran	1·75	20·93
Oats	1·09	12·76
Rape-seed cake	1·72	6·25
Linseed cake	2·62	9·73
Cotton-seed cake	1·72	6·23
Carrots (dry substance)	2·59	8·43
Kohlrübe (ditto)	2·93	6·67

A. G. L.

Linaloe Oil. W. Naumann. (*Chemist and Druggist*, 1906, lxviii., 619.) The following results were obtained on the analysis of three samples of oil shipped direct from Mexico and guaranteed by the shippers to be pure oils :

	No. 1.	No. 2.	No. 3.
Specific gravity at 15° C.	0·8785	0·8800	0·8797
Rotation in 100 mm. tube	− 8° 30′	− 12°	− 11° 10′
Refractive index at 20° C.	1·4635	1·4633	1·4618
Esters	4·3	4·7	4·9
Linalol	66	68	63
Distilling below 190° C.	none	none	
,, ,, 195° C.	7	5	
,, ,, 200° C.	25	35	
,, ,, 205° C.	45	40	

These results are similar to those obtained by Parry and Bennett (ANALYST, 1906, 201), and accordingly the above oils belong to the best class now obtainable.

W. P. S.

On the Chemical Examination of Kerosine. K. Charitschkow. (*Best. ik ....*, vii., 14 : through *Chem. Zeit.*, 1906, xxx. [*Rep.*], 112.) Dehnstedt and Geisler have recently shown the presence of neutral sulphuric esters in various petroleum oils imported at Hamburg. The author now shows that similar esters are sometimes present in Russian petroleum, the quantity varying inversely with the amount of acid used in the purification of the oil. The esters may be recognised by treating the oil with aniline, aniline sulphate being insoluble in kerosine. On burning oil containing sulphuric esters, sulphurous and sulphuric acids are formed and the lamp-wick is charred.

A simple method of determining sulphur in petroleum consists in distilling it over potassium, potassium sulphide being formed and determined in the usual manner. The quantity of unsaturated hydrocarbons present in kerosine should always be determined, as they yield a flame of unpleasant colour. A. G. L.

Collaborative Work on Tannin Analysis. F. H. Small. (*Journ. Soc. Chem. Ind.*, 1906, xxv., 296-298.)—The American Leather Chemists' Association have formulated the following methods for the estimation of tannin in raw materials and analysis of the tannin solutions obtained therefrom. The material is ground to a specified fineness, and the tannin extracted in a copper Soxhlet apparatus so constructed that the extractive is removed from the action of heat, as prolonged boiling of the liquor converts part of the tannin into some compound not tannin, probably gallic acid. The analysis of the tannin solution is conducted on a solution containing 0·35 to 0·45 gram of tannin per 100 c.c. The residues obtained from the evaporation of 100 c.c. each of the solution before and after filtration give the amounts of total and of soluble solids respectively. The tannin is removed from another portion of the solution by treatment with hide-powder, which is then filtered off, and the clear

filtrate evaporated to dryness, the residue being the soluble non-tannins. By deduc-
ing these from the total soluble matter the proportion of tannin is readily obtained.
The hide-powder employed is first treated with a dilute solution of chrome alum,
washed free from uncombined salts, excess of water squeezed out, and the moist
powder added to the tannin solution, a correction being made for the water added
with the hide-powder. Difficulties have arisen owing to failure to obtain clear
filtrates, and to the retention of part of the tannin by the filter-paper, but if
following prescribed conditions concordant results are obtainable. To avoid decom-
position during evaporation and drying of the residues, a special copper steam-bath
has been devised, with a solid top on which the dishes rest, and fitted with a steam-
jacketed cover provided with openings for ventilation.　　　　　　W. H. S.

Analysis of Ebonite Articles. R. Thal. (*Chem. Zeit.*, 1906, xxx., 499.) As
supplied to the Russian army medical service, ebonite cases for instruments and
bottles must fulfil the following requirements : The ebonite must be made from best
Para rubber and sulphur. The quantity of the latter may vary from 27 to 30 per
cent., but should preferably be 29 per cent. The vulcanization must be even
throughout, and the ebonite must be free from surrogates. The amount of ash must
not exceed 0·60 per cent. On warming the ebonite with fuming nitric acid, a clear or
nearly clear solution should be obtained. The material should be black, capable of
being polished, and be free from cracks, indentations, porous or coloured spots, etc.;
it must be sufficiently hard, and yet not too brittle to be worked by tools. The cases
must not break or crack on allowing them to fall by their own weight when empty on
to a stone floor, or on knocking them together.

The analysis of ebonite is carried out by the methods usual for rubber. Moisture
may be determined by drying for two hours at 100° to 105° C. ; longer drying results
in oxidation of the material. For the test with fuming nitric acid, 0·5 gram of the
ebonite in small pieces is gradually added to 20 c.c. of the acid, and the whole is
warmed until nitrous fumes are driven off. A turbid solution indicates an amount of
ash greater than 0·6 per cent. In testing for surrogate, a correction must be made
for the weight lost by the filter-paper on treatment with 8 per cent. alcoholic caustic
soda. The author has previously found this to be 5·5 per cent. For accurate work
corrections must also be made for the amount of sulphur extracted from, and the
quantity of soda retained by, the dried residue.　　　　　　　A. G. L.

Grading of Glues and Gelatines. J. Alexander. (*Journ. Soc. Chem. Ind.*,
1906, xxv., 158-161.)—The author recommends the determination of the reaction to
litmus, viscosity, grease, foam, "set," jelly strength, adhesive strength (under actual
working conditions), and keeping properties. The viscosity is measured by noting
the time of efflux at 80° C. from a 45 c.c. pipette of solutions containing 25 grams of
glue in 100 c.c. of water. The effluent tube is 7 cm. long, and has external and
internal diameters of 9 and 6 mm. respectively, the smallest diameter of the outlet
being about 1·5 mm. The length of the bulb is 9·5 cm., and its outside diameter
3 cm. The amount of grease is approximately proportional to the spots appearing
when the glue solution is painted on white paper with a little aniline or dry colour

Foam is estimated comparatively by agitating with a rod or mechanical agitator, and " set " is the speed with which the jelly hardens. Jelly strength is well measured by pressure with the finger-tips; but a special instrument, more reliable than the shot test, has been devised for the purpose, consisting of a brass cylindrical vessel supported like a gas-tank by four vertical rods, against which it slides with almost frictionless roller-bearings. This rests on a truncated cone of jelly, and shot are poured in until a definite expression of jelly is observed, two vertical brass uprights 5 cm. high connected with an electric-bell circuit being placed beneath the cup, so that when this reaches their level the bell rings. Keeping properties are observed by exposing the uncovered glue solutions for some days at room temperature. An arbitrary series of standards has been devised, based upon the viscosities, sixteen nearly equidistant grades having values assigned of 10 to 160, 10 points being allowed between each grade. The grades specially adapted for particular purposes are mentioned. W. H. S.

Conditions affecting the Foaming and Consistency of Glues. S. R. **Trotman and J. E. Hackford.** (*Journ. Soc. Chem. Ind.*, 1906, xxv., 104 107.) Foaming of glue is increased by overboiling, by prolonged boiling with alkalies, and by the presence of peptones, of soda or lime, of soap beyond a certain limit, of carbolic acid, and of suspended matter. From the influence of the last-named, loaded glues, such as Russian, may be expected to give considerable foam. The amount of foam is reduced by rise of temperature, by the addition of lubricating, bone, or cod oil, or of hydrochloric, sulphuric, acetic, salicylic, or oleic acid. The mineral constituents of water used in glue-making would not affect the quality of the resulting glue. The consistency of glue is not injured by small quantities of peptone so long as they do not replace albumose nitrogen, but is seriously reduced by alkalies and acids, though in a less degree by small quantities of carbolic or boric acid. A small amount of soda or potash soap does not diminish the consistency. The foaming has been measured by means of a graduated tube about 70 cm. long, and of such diameter that each division is 1 cm. in length and has a capacity of 1 c.c. This is half filled with a 10 per cent. solution of the glue, placed in a water-jacket at 60° C., and after allowing the glue solution to attain this temperature, withdrawn, and the level of the solution adjusted to zero. The tube is then corked and shaken vigorously for one minute, replaced in the water-jacket, and the height of the foam read off. Consistency has been determined by noting the time taken by spheres to fall through a column of the given glue solution. H. J. Watson (*ibid.*, 1906, xxv., 209-211), from independent experiments on the same lines, concludes that foaming is not materially increased by the presence of free alkali or acid, except sulphurous acid. Mucins increase the foam, and zinc sulphate lengthens the time it takes to die away, but heat appears to be the all-important factor in producing foaming glue, probably due to hydrolysis of the gelatin to gelatone. By reducing the period under heat to the shortest possible, practically foam-free glue should be obtained. This author measures the foam by shaking 50 c.c. of a 10 per cent. solution of the glue at about 50° C. in a stoppered graduated cylinder 2·5 cm. in diameter, and reading the height of the top of the foam as soon as the height of the solution reaches 45 c.c. W. H. S.

The Determination of Urea. B. Glassmann. (*Berichte*, 1906, xxx. 705-710. —The following modification of Liebig's and Pflüger's methods is claimed give very accurate results, and to be more easily applied than any other meth The urea is precipitated from the solution, which has been neutralized with sodi carbonate, by means of a known excess of standard solution of mercuric nitrate, precipitate filtered off, the filtrate acidified with nitric acid, and the excess of mercury determined by titration with $\frac{N}{10}$ ammonium thiocyanate solution, iron ammonium sulphate being used as indicator. From the amount of mercury that has been take up the urea is calculated by means of the equation—

$$2CON_2H_4 + 4Hg(NO_3)_2 + 4H_2O = [2CO(NH_3)_2 + Hg(NO_3)_2 + 3HgO] + 6HNO_3.$$
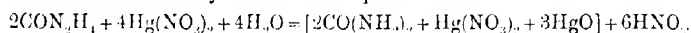
The conditions for the determination of the urea in urine by this method are t same as those required in Liebig's original method—viz. : (1) The urine must contain more than traces of albumin, which otherwise must be precipitated w acetic acid. (2) It must not be in full alkaline fermentation. (3) It must contain leucine or tyrosine. (4) It must not contain abnormal amounts of alk chlorides, bromides, or iodides, or of benzoic, salicylic, or hippuric acids. (5) If darkly coloured it should be treated with animal charcoal. C. A. M.
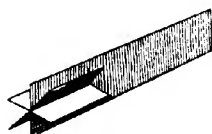
Simplified Ultimate Analysis for Technical Purposes—II. M. Dennstedt. (*Zeits. angew. Che* 1906, xix., 517 ; *cf.* ANALYST. xxx., 135, 348, and this vol. 122.)—The author has given up the use of platinized quart which occasionally scratches the combustion-tube, and no uses rolled-up pieces of platinum foil, or, better, platinum foil " stars " (Fig. 1), weighing 1 or 2 grams, which m be obtained from Hereaus, of Hanau. For the introduction of the double curre
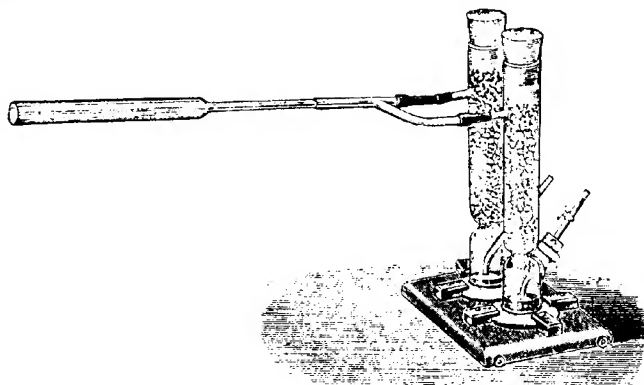

Fig. 1.

Fig. 2.

of oxygen, the arrangement shown in Fig. 2 is recommended, as it very seldom requires renewal. A. G. L.

INORGANIC ANALYSIS.

On the Quantitative Determination of Arsenic by the Marsh Method.
G. Bertrand and Z. Vamossy. (*Ann. Chim. Phys.*, 1906, 523; through *Chem. Zeit.*, 1906, xxx. [*Rep.*], 141.)—The method gives good results, provided that the authors' instructions (*Ann. Chim. Phys.*, 1903, 242) are used with the modification that a length of 40 cm. of the tube is heated and that the tube has a bore of 2 mm. For quantities of 0·01 gram arsenic and more, the gas, after leaving the apparatus, is passed through a solution of silver nitrate. The arsenic mirror should be dissolved in sodium hypochlorite and not in nitric acid. A. G. L.

On a Method for the Detection of Very Small Quantities of Yellow Phosphorus. R. Schenck and E. Scharff. (*Ber.*, 1906, 1522; through *Chem. Zeit.*, 1906, xxx., [*Rep.*], 156.)—Yellow phosphorus, even in very small quantities, ionizes air, and hence may be made to discharge an electroscope; phosphorus trisulphide, even when luminescent, does not possess this property, and does not yield any phosphorus trioxide on slow combustion at moderate temperatures. The authors make use of the apparatus shown for the detection of small amounts of yellow phosphorus. By means of a tube passing through the ground-glass stopper of the tube (*a*) a slow current of air is led over the substance to be examined, which is placed at the bottom of the tube. The air then passes through the vessel (*c*), which communicates by means of its removable stopper (*d*) with an electroscope (*b*). A piece of sodium in the tube (*e*) serves to keep the electroscope dry and sensitive. A. G. L.
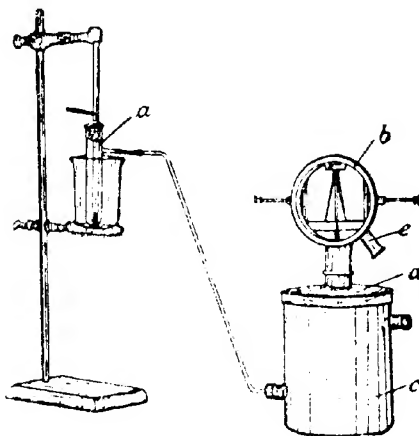
Determination of Small Quantities of Copper in Water. E. B. Phelps. (*Journ. Amer. Chem. Soc.*, 1906, xxviii., 368-372.)—The copper is separated electrolytically from an acid solution, dissolved in dilute acid, and, after neutralizing, determined colorimetrically as sulphide. Sufficient water to contain 0·1 to 1·0 mgm. of copper is evaporated to 75 c.c. and washed into a platinum dish, which serves as anode, adding 2 c.c. of dilute sulphuric acid for clear and soft waters, 5 c.c. for those rich in organic matter or clay. The cathode, consisting of a flat spiral of stout platinum wire, is then suspended in the solution parallel to and about ½ inch from the bottom of the dish, and the circuit closed. After electrolysing for four hours with occasional stirring, using a current of 0·02 ampère, the cathode is removed without

first opening the circuit and immersed in dilute nitric acid previously heated to boiling. The spiral is washed and the liquid evaporated to dryness on the water-bath, a few drops of hydrochloric acid being added if silver is suspected. The residue is then dissolved in water, washed into a Nessler glass, made up to 100 c.c., and 10 c.c. of an alkaline solution of potassium sulphide, prepared by mixing equal volumes of 10 per cent. potash solution and a saturated aqueous solution of sulphuretted hydrogen, added. A similar tube is prepared by adding 10 c.c. of the reagent to a tube of distilled water, and then running in, 0·2 c.c. at a time, a standard solution containing 0·2 gram copper per litre. This method gives good results in the presence of sewage and industrial waste, iron, lead, silver, and tin, and in highly-coloured surface-waters.   W. H. S.

APPARATUS.

Apparatus for the Continuous Registration of the Results of Gas Analysis and Precipitation in Liquids. (*Chem. Zeit.*, 1906, xxx., 347.) B Stollberg has patented (in Germany) the apparatus shown in the figure. It consists
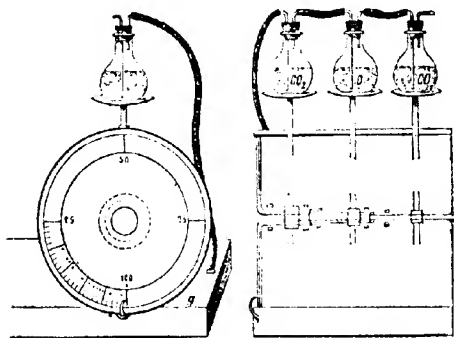
essentially of a number of flasks, containing suitable reagents, connected with each other and mounted on separate pendulum - balances, which rotate graduated paper discs at speeds corresponding with their weights. On these discs a pencil worked by clock-work marks off minutes. By means of a pump (not shown) worked by a falling-weight mechanism determined quantities of the gas (from a chimney, etc.) to be analysed are drawn through the flasks, and the increase in weight of each flask in a given time is read off from the discs. By means of suitable modifications the apparatus may also be made to give a continuous record of the specific 'gravity of a liquid, the amount of suspended or precipitated matter in it, and the like.   A. G. L.

Modified Westphal Balance for Solids and Liquids. F. M. Williams. (*Journ. Amer. Chem. Soc.*, 1906, xxviii., 185-187.)—The balance is adapted for solids, particularly cements and minerals, by lengthening the pointer, upon which, at a distance equal to the length of the other arm, is suspended a support carrying two pans, one above, the other below, the surface of the liquid, by means of which the object may be weighed first in air, then in the liquid. A two-piece counterpoising weight movable along the threaded portion of the pointer facilitates adjustment, and a cam device for raising the beam and locking it in place tends to prevent wear upon

the knife edges. The insertion of a hinge-joint in the upright standard arm allows the instrument to be folded up within a small space. W. H. S.
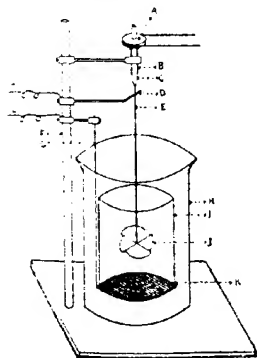
A Burette Top for the Absorption of Carbon Dioxide and other Gases (*Chem. Ztg.*, 1906, xxx., 156. Gustav Muller, of Ilmenau, has devised the apparatus shown, which is designed to prevent the absorption of carbon dioxide by caustic alkali solutions in the burette. The apparatus fits in the top of the burette, which is widened to admit it, by means of a ground-glass joint. It contains a solution of caustic alkali, through which any air entering the burette has to bubble, the path of the air being shown by the arrows. A piece of solid potash may also be placed in the bulb (*d*). In filling a burette for the first time with the standard solution, the apparatus is placed on the top of the burette and filled with potash. It is then turned so that a groove (*f*) at the ground-glass joint is opposite a hole (*g*) in the burette. The standard solution is then run in from below, the air from the burette escaping through (*g*). The top is then turned so as to shut off communication between (*g*) and (*f*), and kept in this position. Any air entering the burette has then to bubble through the potash, whilst in filling the burette afresh the potash is simply forced up into the bulb (*d*).

A. G. L.

A New Electrolytic Apparatus. S. F. Acree. (*Amer. Chem. Journ.*, 1906, vol. 35, pp. 313-316.)—The essential feature of the apparatus is that by means of a rotating, propeller-like anode all the liquid is continually circulated through the cathode K, which is of platinum gauze, 50 meshes to the linear inch, and consists of an outer ring 2·5 inches in diameter, forming one piece with the arm G, and an inner removable ring which holds the gauze in position, the two rings being kept firmly together either by fine platinum wire or by four small drops of gold. The arm G is held in position by a binding-screw attached to the glass rod F, and supports K half an inch above the bottom of the beaker H. A glass cylinder, I, rests on the outer ring of K, its upper edge being at least a quarter of an inch beneath the surface of the liquid. The anode J, of heavy platinum foil, is riveted to the platinum rod E, which is sealed into the glass tube C, and the latter rotated in the glass tube B by means of a pulley, A, and a Rabe water turbine or a small electric motor. A platinum strip or stout wire, D, connected to a binding-screw on F brushes against E, making good contact. The distance between J and K is adjustable, and depends entirely upon the voltage and strength of current required.

W. H. S.

New Form of Potash Bulbs for Estimation of Carbon Dioxide from **Combustions. S. F. Acree.** (*Amer. Chem. Journ.*, 1906, vol. 35, pp. 309-311.)— A modification of Soxhlet's alkali apparatus, in which the two bulbs B and D are filled and surrounded with glass wool saturated with 50 per cent. KOH solution, the mixture of gases from the combustion tube being thereby brought in contact with a very large surface of alkali solution, insuring almost perfect absorption. The glass wool around the bulbs is kept in position by four small glass projections E, which extend from the lower bulb nearly to the wall of the outer vessel, and the exit tube from the lower bulb dips into the potash solution F. A calcium chloride tube is attached by means of a ground-glass joint at A. The efficiency of the apparatus is proved by the fact that on passing through two of them in series (a) a stream of nearly pure CO_2 for fifteen minutes, (b) a mixture of one-third CO_2 and two-thirds air, in neither case was the amount of CO_2 absorbed by the second apparatus as much as 0·10 mgm. W. H. S.
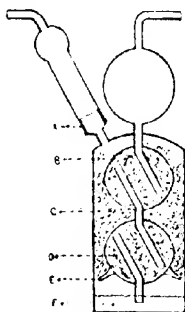
Porcelain-lined Bomb for General Laboratory Use. S. F. Acree. (*Amer. Chem. Journ.*, 1906, vol. 35, p. 309.)— The bomb E is of soft steel, about $\frac{3}{4}$ inch thick, and tested to 250 atmospheres water pressure, its entire inner surface up to the threads at the neck being lined with white porcelain $\frac{1}{16}$ inch thick, which may be of acid or of alkali-proof material. The stopper B is of hard bronze, has a square head, and screws into the neck of the bomb with heavy threads, the ring C, of very hard rubber or lead, making a gas-tight joint. The handle I, attached to the screw A on a square head, serves as a valve, the screw fitting into the stopper with gas-tight threads and packing, and having a tip, D, of very hard rubber or lead, which closes the bomb so tightly that liquid carbon dioxide cannot escape. The inlet or outlet G has a cap, and is threaded to fit carbon dioxide cylinders. The bomb rests in a detachable ring base, H.
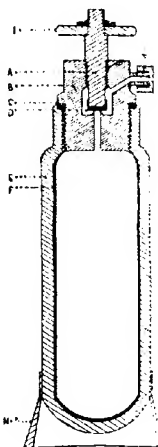
W. H. S.
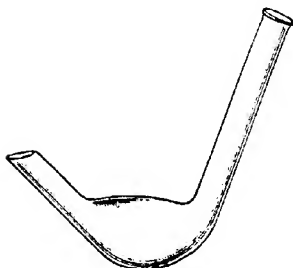
Dougal Assay Tube.—This, which is a modified flask, will be found useful for "parting," dissolving metals, minerals, etc., solution proceeding quietly, as the double opening provides a free escape for the evolved gases. The apparatus may be obtained from Messrs. J. J. Griffin and Sons.

W. J. S.

A New Rheostat for Electrolytic Analysis.
G. Pascalis. (*Mon. Scient.*, 1906, 4 Ser., 20, 168; through *Chem. Zeit*, 1906, xxx. [Rep.], 104.) The small adjustable resistance shown in the figure on the top of the electrolytic stand has been designed by the author in conjunction with Grésy. Its height is only 80 to 100 mm., the diameter being 50 to 60 mm. A casing protects it from fumes. By means of the screw on the 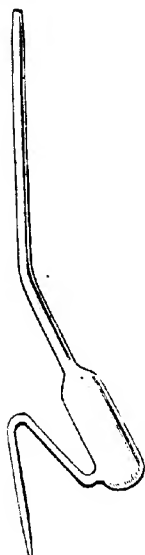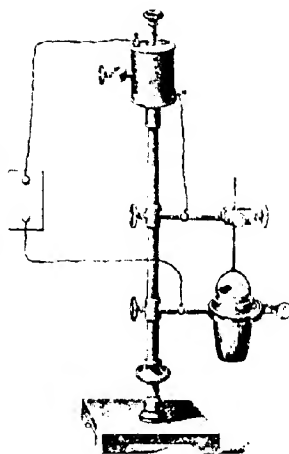top the strength of a current at 4 to 6 volts may be regulated from 0 to 1 ampère in $\frac{1}{10}$ ampère stages.   A. G. L.

Struthers Syphon Pipette possesses the following advantages—compactness, less danger of liquid pipette being sucked up into the mouth, no necessity for using tip of finger in stopping flow, mark more exactly and easily caught, easy regulation and stoppage of flow, which is effected by simply tilting the pipette; it always discharges the same volume, as the bulb completely empties itself. The pipette is manufactured by Messrs. J. J. Griffin and Sons.

W. J. S.

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REVIEWS.

THE CYANIDE INDUSTRY. By R. ROBINE and M. LENGLEN. Translated by J. ARTHUR LECLERC, PH.D. With an Appendix by C. E. MUNROE, PH.D. (New York: Wiley and Sons. London: Chapman and Hall, 1906. Price 17s. net.)

The manufacture and utilization of cyanogen compounds have undergone rapid development in recent years, and the work under review is an attempt to classify the various methods employed at the present time. The book comprises four subdivisions, the first of these dealing with the chemical reactions involved, together with the preparation and properties of the more important single and double cyanides. Part II. is practically a directory of the works at which the cyanide industry is carried on, whilst Part III. is devoted to the manufacturing processes in general use.

The commercial application of the different cyanogen compounds is discussed in the last section, and an appendix contains a digest of the United States patents relating to the recovery of precious metals by means of cyanides.

The descriptive matter as a rule is concise, and the processes of manufacture are clearly explained. The authors point out that the application of cyanides to the treatment of auriferous materials is the immediate cause of the progress realized in the industry during the last fifteen years, whilst the discovery of cyanide compounds in the bye-products of the manufacture of illuminating gas has also widened the field of investigation towards synthetic processes.

In the small space allotted in the book to analytical properties the usual tests for cyanides are included, but the information given in reference to quantitative determinations is rather meagre.

Although the book will probably prove useful to the manufacturer as a resumé of the ordinary methods employed in the production of cyanides, its value to the analytical chemist is somewhat problematical. P. A. E. R.

LES INDUSTRIES DE LA CONSERVATION DES ALIMENTS (The Food-preserving Industry. By X. ROCQUES. (Paris, 1906. Pp. xii + 506. Price 15 francs.)

This book is divided into seven chapters, respectively treating of historical sketch, the causes and effects of changes due to putrefaction, preservation by heat, by cold, by desiccation, by antiseptics, and by the prevention of the entrance of micro-organisms into such naturally sterile products as eggs.

There is little or no analytical information, the whole subject being treated from a technical point of view; but the work is well up to date, and gives a fairly complete description of the various methods of food preservation. As is natural in a French work, the processes and details of packing and transport are chiefly those used in France, but these are fairly typical, and in most cases will give the food analyst a good general idea of the technology of the food-preserving industry.

One passage taken from the report of Dr. Bordas, adopted by the Congress of Hygiene, is worth quoting *in extenso* :

" En résumé, l'addition d'antiseptiques dans les denrées alimentaires produit les resultats suivants :

" 1. Elle est susceptible de nuire à la sante.

" 2. Elle peut permettre de conserver des éléments ayant déjà subi un commencement d'altération.

" 3. Elle modifie le plus souvent la composition des éléments organiques.

" *Il y a lieu d'interdire l'emploi des antiseptiques quels qu'ils soient, nocifs ou non dans toutes les matières alimentaires.*" H. D. R.

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

ON THE PRESENCE AND DETECTION OF CYANOGEN IN JAVA, BURMA, AND HARICOT BEANS.

By R. R. TATLOCK AND R. T. THOMSON.

(*Read at the Meeting, May 2, 1906.*)

As we had to deal with this question in the recent poisoning of cattle by "Java" beans, we have thought it might be of interest to put on record the result of our examination for cyanogen compounds of "Java" and other beans, as well as of peas of various kinds. As a fairly full report with regard to the poisoning cases in Scotland is given in the March and April numbers of the *Journal of the Board of Agriculture*, we shall not refer further to these, nor, indeed, to anything directly connected with them, but shall confine our attention to the various specimens which we procured for experiment.

For the determination of cyanogen we employed the method which Professor Dunstan used — namely, extracting the glucoside with alcohol, distilling off the latter, decomposing the former with hydrochloric acid, and distilling off the hydrocyanic acid (the *Agricultural Ledger*, No. 2, 1905). For the detection of the hydrocyanic acid we made a mash of about 10 grams of the ground beans with 20 or 30 c.c. of warm water in a small stoppered bottle and kept at 40° to 50° C. for half an hour, then applied a modification of the Schönbein test. This consisted in holding in the vapour in the bottle a piece of filter-paper, which had been first dipped in a 0·2 per cent. tincture of guaiacum resin, and then in a 0·1 per cent. solution of copper sulphate, when the paper assumed a fine blue colour almost immediately, if hydrocyanic acid was present. It is important that the blue colour should be rapidly developed, as the prepared paper slowly assumes a blue tint when exposed to the air, and this might be mistaken by careless observers for the effect of hydrocyanic acid. A good plan, therefore, is to prepare two slips of paper simultaneously, insert one into the vapour to be tested for hydrocyanic acid, and simply expose the other to the air, when a comparison will decide the question. If this plan is adopted no mistake can be made. In applying the Schönbein test it is generally directed to dip the filter-paper in a 10 per cent. tincture of guaiacum resin, and dry before dipping in the 0·1 per cent. solution of copper sulphate. On drying the paper, however, it

always assumes a blue tint, and this vitiates its application to the detection of hydrocyanic acid. In consequence of this defect we have modified the test as described above.

It should be noted that, as a rule, hydrocyanic acid (if present) can be detected after half an hour's warning; but where no positive result is obtained, the bottle should be closed and allowed to stand at the ordinary temperature for several hours in order to allow the hydrocyanic acid to accumulate by the gradual action of the enzyme contained in the bean on the cyanogenetic glucoside.

After deciding the method of procedure, we, in the first place, examined several specimens of Java beans, and found from 0·027 to 0·137 per cent. of hydrocyanic acid, this being, of course, understood to exist in the beans in the form of an amygdalin-like glucoside. These results practically agree with those of the uncultivated variety examined in the Scientific and Technical Department of the Imperial Institute. In order to determine whether there was really any difference as regards cyanogen contents in beans of different colour, we obtained an average sample, weighing about 3 pounds, of a lot of Java beans, and separated them into five different kinds. These consisted of white, brown of various shades, speckled, chiefly brown and white, with a few purple and white, purple of various shades, and black beans. The sample was composed of these as follows :

							Per Cent.
White beans	...	...	...	...	...	...	9
Brown beans	...	...	...	...	...	...	34
Speckled beans	...	...	...	. .	...	...	33
Purple beans	...	...	...	...	...	...	20
Black beans	...	...	...	...	...	...	4
							100

These were tested separately with the following results :

							Hydrocyanic Acid. Per Cent.
White beans	...	...	...	...	...	...	0·027
Brown beans	...	...	...	...	...	...	0·038
Speckled beans	...	...	...	. .	...	...	0·038
Purple beans	...	...	...	...	...	...	0·031
Black beans	...	...	...	...	...	...	0·012
Average	...	...	...	...	...	...	0·036

From these results alone it might appear that the white variety contained the least, and the black the most, hydrocyanic acid ; but this distinction does not really hold good, although it has been held that white contains the least, and purple the most, of that ingredient. Other tests we have made showed in brown beans 0·07, and in black beans only 0·029 per cent. of hydrocyanic acid, so that the generalization as to the quality of the bean according to its colour is of no value whatever.

It has been stated that the cyanogen was contained in the husk and not in the kernel of the bean, but this opinion or assumption we have proved to be quite untenable. We carefully decorticated a small specimen of black beans, and found

that the husk was equal to about 10 per cent. of the whole, while the percentage of hydrocyanic acid in the decorticated portion was 0·030 per cent., and that in the husk only 0·003 per cent. We also procured a large specimen of decorticated beans, and the corresponding husks, from the mixed varieties, and found in the decorticated portion 0·061, and in the husks 0·006 per cent. of hydrocyanic acid. It is thus apparent that the kernel contains at least ten times as much hydrocyanic acid as the husk, so that the statement we have referred to is not borne out by fact. It has also been suggested that it is the small, rounded beans that contain the hydrocyanic acid, but our experience does not bear this out even in the slightest degree.

Having dealt with the Java beans, we next procured specimens of various kinds of bean and pea, and tested them for hydrocyanic acid. with the following results, which include also the average weight of the beans :

	Hydrocyanic Acid. Per Cent.	Number of Beans in 100 Grams.
English beans	none	... 170
Morocco beans	none	...
Smyrna beans	none	... 100
Java beans	0·027 to 0·137	.. 272
Rangoon or Burma beans	0·005	... 368
Large haricot beans	none	... 61
Large haricot beans	none	... 78
Small haricot beans (Rangoon) ...	0·009	... 384
Small haricot beans	0·006	120
Small haricot beans	0·001	... 448
Small haricot beans (Chili)	none	... 228
Paiyin beans	none	... 1960
Gram	none	... ..
Calcutta white and gray peas ...	none	... ..
Odessa and Mutter peas	none	...

The haricot beans (both small and large) mentioned above were obtained from different sources, and were all sold for human food. The sample containing 0·001 per cent. of hydrocyanic acid was purchased by ourselves in a grocer's shop in Glasgow.

From the above table we have further and most conclusive proof that it is a mistaken idea that the white bean is free from the cyanogen compound, as the latter was present in three specimens of the white haricot bean, which is almost certain to be a cultivated variety. It will be observed that the specimen of the ordinary (or coloured) Rangoon or Burma bean given above contains only rather more than half that contained in one specimen of the small white haricot beans.

In conclusion, we may note the effect of boiling the unground beans with water, and of mashing the ground beans with warm water. In carrying out the former experiments the three samples of small haricot beans containing hydrocyanic acid were steeped overnight with water and boiled until thoroughly cooked. They were then allowed to cool, beaten up with water, and the modification of Schönbein's test applied, but hydrocyanic acid could not be detected in any of them. The hydrocyanic acid was now determined in the beans originally containing 0·009 per cent., after this treatment, and 0·002 per cent. was found. These results show clearly that a large

proportion of the cyanogen compound and the whole of the enzyme have been destroyed by the boiling, but whether the amygdalin glucoside is harmless, seeing there is no enzyme present to produce hydrocyanic acid, is a question with which we cannot deal. In order to corroborate these results, Java beans containing 0·03s per cent. of hydrocyanic acid were steeped and boiled in the manner described ; but after this treatment no hydrocyanic acid could be detected by the modification of the Schönbein test, although 0·019 per cent. in the form of the glucoside was actually present.

The result is entirely different when cold or warm water, as applied in the test referred to, is mixed with the ground bean. In this case we found that in two or three days practically the whole of the cyanogenetic compound was decomposed, and the cyanogen in it liberated in the form of hydrocyanic acid.

DISCUSSION.

Dr. VOELCKER remarked that Professor Dunstan drew a clear distinction between the white and the coloured beans, and spoke of the white beans as being cultivated and as containing no cyanogenetic glucoside, whereas the speckled and purple beans did contain one. He was inclined to think, however, that this was an assumption rather than the result of actual experiment, and accordingly the present paper, if the beans dealt with were botanically the same, would be of considerable value.

Mr. HENDRICK said that he had had occasion to examine a good many samples of these Java beans, and had done a little investigation on lines somewhat similar to part of that recorded in this paper. His results, generally speaking, were in accord with those of the authors. Every specimen that he had examined of these so-called Java beans, a great many thousands of tons of which had been imported into Europe during the last year or two, had yielded hydrocyanic acid in relatively large quantity. The beans varied very greatly in colour, even from bag to bag of the same consignment. In some cases white beans were more numerous than those of any other colour; in other cases the majority of the beans were black. He did not find, however, any corresponding variation in the amount of hydrocyanic acid, though, generally speaking, the darker beans contained a little more hydrocyanic acid than the light ones. He was not satisfied that the whole of the hydrocyanic acid which it was possible to produce from the beans was obtained by extracting the glucoside with alcohol, which was, he understood, the method used by the authors of this paper. In a few experiments which he had made he had found that mere soaking of the ground beans in water and subsequent distillation yielded, in every case that he had tried, a larger quantity of hydrocyanic acid than was obtained by the alcohol extraction method. He also had de-husked a sample of the beans, and had not obtained any hydrocyanic acid from the husks ; it was all contained in the inner part of the beans. It had been stated that where the beans had been washed before being used there had been no poisoning. Through the kindness of certain large dealers he had been able to visit some mills where the beans were thus treated, and had seen the whole process. The washing process was a very brief one, and though it removed much dirt, it did not do more than clean the outside of the bean, and could not affect the amount of cyanogenetic glucoside present. His difficulty was to

explain why there had not been far more cases of poisoning. Great quantities of the beans had gone into consumption. He personally knew of cases in which beans, of which samples from the same parcel yielded a large proportion of hydrocyanic acid, had been fed daily for weeks to cattle without ill-effect. In other cases poisoning had occurred at once, and large numbers of animals were lost. The poisoning seemed to be, so to speak, sporadic, and he felt convinced we had still something to learn as to its cause.

Mr. Estcourt said that he had been told by a miller near Manchester of certain beans which had poisoned a considerable number of cattle. These beans were described as " Indian mutter."

Mr. Hendrick said that he had examined what were known as " mutter peas," and had not found them to yield any hydrocyanic acid. It was known, however, that these peas sometimes caused poisoning of a different kind (see a paper by Dr. J. A. Voelcker, Analyst, xix., 102). In some cases the beans had been given in the form of dry meal, in some cases they had been soaked, and in some cases steamed. He had always found it quite easy to detect the hydrocyanic acid in these beans by smell, after soaking the meal in water for a short time.

Dr. Leather said that there was no doubt that these various beans, those from Burma especially, did contain a cyanogenetic glucoside, though it was not yet certain whether this was identical with the phaseolunatin of Professor Dunstan. It is uncertain, also, what the exact botanical nature of these beans is. They seem to be a mixture of species, but in India nearly all the crops are mixed. He thought, from what he had seen of these beans, that they probably all belong to the same genus, but it was not certain whether Professor Dunstan's statement as to *Phaseolus lunatus* is generally correct. Probably it is correct for the plant that Professor Dunstan operated on, but it is not certain that all these Burmese beans are the same. He had found a cyanogenetic glucoside in various Indian beans, and its presence seemed to be very common in leguminous plants in the East. The quantity of prussic acid obtainable varied considerably. It is very much to be desired, of course, that further knowledge should be obtained as to the physiological action of the glucoside itself. It is easy to understand the production of prussic acid by grinding up and soaking the beans in water, because these cyanogenetic glucosides are almost always associated with enzymes capable of hydrolysing them; but whether such hydrolysis would necessarily be brought about by the enzymes of the digestive organs is another question altogether, and, as far as he was aware, no work has been done in that direction. It seems very possible that the erratic effects of the beans might be explained by variations in the degree to which hydrolysis results from digestive action. In one of the first references made to him in relation to these Burmese beans, it was stated that the beans were consumed regularly by the prisoners in Burmese prisons. All that food was cooked, so that the enzyme in it was certainly destroyed; and it remained then for the enzymes of the digestive juices to hydrolyse the glucoside if they could. Apparently, as a rule, they could not. In the case of stock-feeding it is clearly necessary that such beans shall first be cooked, so as to destroy the enzyme; but it is to be recollected that the glucoside is not destroyed by a temperature of 100° C.

Mr. HENDRICK asked whether Dr. Leather knew of any case of poisoning from Burma beans.

Dr. LEATHER said that he only knew of cases of poisoning that had occurred in this country; none had occurred in India.

Mr. HENDRICK said that, as far as he knew, there had been no case of poisoning by Burma beans. It was at first stated in the newspapers that some of the beans which had caused poisoning were from Burma, but in every case, so far as he was aware, it was found on investigation that they were Java beans. The latter were different from Burma beans. Both seemed to be varieties of *Phaseolus*, though he did not know the exact species. The Burma beans were quite uniform.

Dr. LEATHER: No, they vary very much indeed.

Mr. HENDRICK said that all the samples which he had seen of what was described as "Red Burma Beans" were red mottled beans, very similar to one another in appearance, whereas the Java beans he had seen varied greatly in colour and appearance. These red Burma beans have been imported in large quantities for many years past, and are extensively used as cattle-food in this country, but he had never heard of an authenticated case of poisoning arising from their use.

NOTE TO DISCUSSION BY THE AUTHORS.—Our experience differs from that of Mr. Hendrick with respect to the extraction of the glucoside with alcohol, as this method gave more cyanogen than that by simply soaking the ground beans with water and distilling.

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ON THE POLENSKE METHOD FOR THE DETECTION OF COCOANUT OIL IN BUTTER.

BY S. RIDEAL, D.SC., F.I.C., AND H. G. HARRISON, M.A., A.I.C.

(Read at the Meeting, May 2, 1906.)

THE Polenske method for the detection of cocoanut oil in butters depends upon two conclusions at which he has arrived:

1. That in the distillation of the fatty acids, the quantity of insoluble volatile acids bears a strict relationship to the soluble volatile acids.

2. That a mixture with cocoanut oil reduces the "soluble" figure, but at the same time increases the "insoluble" figure to such an extent that each per cent. of cocoanut oil gives 0.1 c.c. $\frac{N}{10}$ alkali in excess of the figure obtained from a genuine butter giving the same "soluble" figure.

To test these conclusions a number of pure English butters have been examined, as well as butters of unknown origin. We find that the distillates from pure butters do not give the "soluble" and "insoluble" figures in such a strict ratio, but that, starting with a pure butter fat, and mixing it with cocoanut oil, the relative increase in the "insoluble" figure practically agrees with Polenske's results.

By plotting his " insoluble " figures against " soluble " a smooth curve is obtained and none of the thirty-one points lie far from the curve:

Our butters show much more divergence, but by taking an average curve in the two cases, the English butters give a curve lying considerably below Polenske's, and the curve for the unknown butters lies between the other two. Polenske's highest Reichert-Meissl value is only 30·1, while both the other series give higher values in this direction.

The following results have been obtained by us :

PURE ENGLISH BUTTERS. JUNE AND JULY.

County.	Number of Cows	Pure Butter Fat.		Butter Fat 20 per Cent. Coceanut Oil.	
		Soluble c.c. $\frac{N}{10}$.	Insoluble c.c. $\frac{N}{10}$.	Soluble c.c. $\frac{N}{10}$.	Insoluble c.c. $\frac{N}{10}$.
Devonshire	?	31·2	2·05	26·7	1·0
Huntingdonshire	35	28·9	1·85	26·85	4·0
,,	4	30·95	1·7	27·15	4·0
,,	7	29·35	1·85	26·3	4·25
,,	5 or 6	30·15	1·85	26·3	4·55
,,	several	29·85	1·85	26·55	4·25
Surrey	1	31·6	1·6		—
Somerset	4	34·55	2·15		—
,,	?	29·0	1·7		—
,,	?	30·05	1·8		
Devonshire	?	29·5	1·65		—
Somerset	12	31·25	1·95		—

When the first six of these were mixed with 20 per cent. of cocoanut oil giving "soluble" and "insoluble" values of 8·75 and 13·4, on the average the "soluble" figure was decreased by 3·4 and the "insoluble" figure increased by 2·3.

In order to get an idea of the changes in the values which take place under varying conditions of season, food, etc., samples have been taken at fortnightly intervals from a Huntingdonshire dairy farm since August 14, 1905. These butters are made from the milk of about thirty-five cows, a number sufficiently large to eliminate variations due to period of lactation in the individual cows. In each case the cows were milked within the week preceding the date given.

FORTNIGHTLY SAMPLES FROM SAME DAIRY.

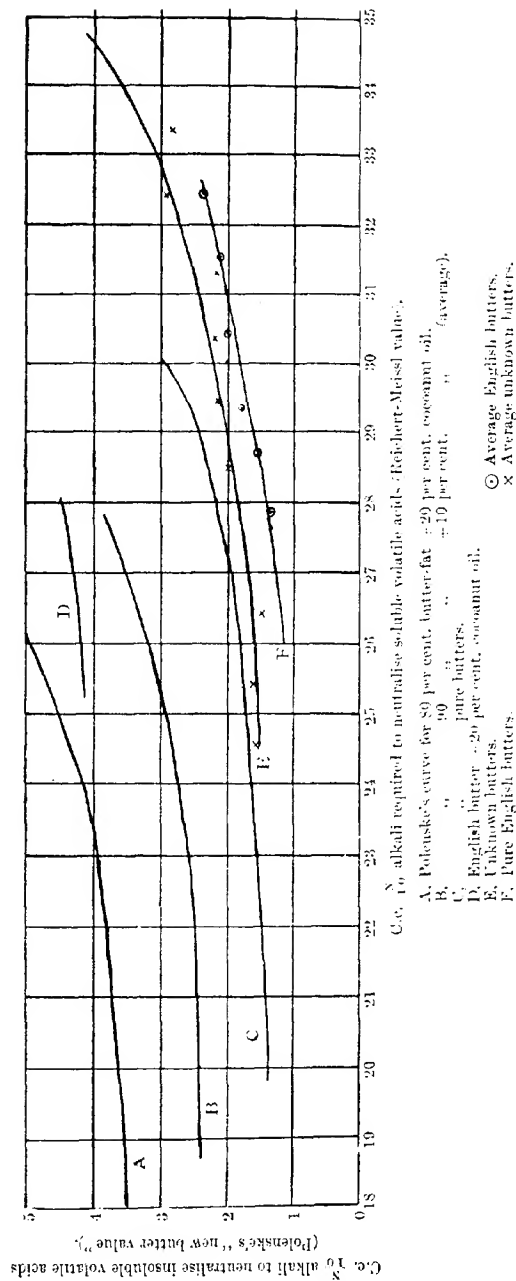| Date.						Soluble c.c. $\frac{N}{10}$.	Insoluble c.c. $\frac{N}{10}$.
June 29, 1905	...	...	...	...	...	28·9	1·85
Aug. 14	,,	...	...	...	...	29·55	1·7
,, 28	,,	...	...	...	...	28·5	1·2
Sept. 11	,,	...	...	...	...	27·95	1·3
,, 25	,,	...	...	...	...	27·8	1·35
Oct. 9	,,	...	...	...	...	29·2	1·35
,, 23	,,	...	...	...	...	32·1	2·3
Nov. 6	,,	...	...	...	...	30·7	2·2
,, 20	,,	...	...	...	...	32·9	2·05
Dec. 4	,,	...	...	...	...	30·1	1·75
,, 18	,,	...	...	...	...	31·75	2·2
Jan. 1, 1906	...	...	...	...	...	30·5	2·1
,, 15	,,	...	...	...	...	30·25	2·25
,, 29	,,	...	...	...	..	31·8	2·1
Feb. 12	,,	...	...	...	...	32·3	2·75
,, 26	,,	...	...	...	...	31·25	2·3
Mar. 12	,,	...	...	...	..	31·8	2·5
,, 26	,,	...	...	...	...	29·05	2·3
April 9	,,	...	...	...	...	30·8	2·4

Until October the cows were entirely on grass and out all the time, then they began to come in at night and have linseed and cotton-cake in addition. During November and December the cows were kept under shelter, and in addition to cake were fed with hay, oatmeal, and rabi. After December mangel-wurzel was substituted for the rabi, and some of the cows began to go out for part of the day.

The average results obtained from all these English butters are given in the curve. They were obtained by taking averages of the results lying within a range of 1 c.c. of soluble volatile acids as given in the following table :

AVERAGE RESULTS FOR PURE ENGLISH BUTTERS.

No. of Samples.	R. M. Values.	Average.	
		Soluble c.c.	Insoluble c.c.
2	27–28	27·88	1·33
2	28–29	28·70	1·53
7	29–30	29·36	1·77
8	30–31	30·44	2·00
7	31–32	31·52	2·10
3	32–33	32·43	2·37
0	33–34	—	—
1	34–35	34·55	2·15

Fig. Polenske's curve for 80 per cent. butter-fat +20 per cent. coconut oil.

C.c. $\frac{N}{10}$ alkali required to neutralise soluble volatile acids (Reichert-Meisel value).

A. Polenske's curve for 80 per cent. butter-fat +20 per cent. coconut oil.
B.   "   "   90   "   +10 per cent.   "   (average).
C.   "   "   pure butters.
D. English butter +20 per cent. coconut oil.
E. Unknown butters.
F. Pure English butters.

⊙ Average English butters.
× Average unknown butters.

C.c. $\frac{N}{10}$ alkali to neutralise insoluble volatile acids
(Polenske's "new butter value").

In a similar manner the figures obtained from one hundred and three unknown butters, presumably genuine, were averaged as follows :

AVERAGE RESULTS FOR 103 UNKNOWN BUTTERS.

No. of Samples.	R. M. Values.	Average.	
		Soluble c.c.	Insoluble c.c.
3	24–25	24·58	1·55
4	25–26	25·46	1·58
7	26–27	26·42	1·46
8	27–28	27·27	1·73
19	28–29	28·50	1·98
29	29–30	29·45	2·12
20	30–31	30·36	2·16
6	31–32	31·30	2·13
4	32–33	32·41	2·91
2	33–34	33·35	2·83
1	34–35	34·7	4·1

During the same period margarines were examined in the same way, but in no case gave an " insoluble " value greater than 1 c.c. $\frac{N}{10}$ alkali ; and mixtures made with butter, margarine, and cocoanut oil gave figures which indicated the amount of cocoanut oil present, but no indication in themselves of margarine if a butter of high Reichert value were taken.

Cheese fats examined by the same method, while giving, as is well known, the Reichert value higher than is general with butters, gave " insoluble " values which are in the same ratio to the " soluble " values as in the case of butters.

DISCUSSION.

The PRESIDENT (Mr. Bevan) asked whether the saponification was done with glycerin or with alcohol. The Polenske number, as was well known, differed considerably according to whether glycerin or alcohol was used, being, if he remembered rightly, higher with glycerin than with alcohol.

Mr. HARRISON said that glycerin had been used, following the process as prescribed.

Mr. E. R. BOLTON said that he had been particularly interested in this paper in so far as it related to cocoanut oil, with which he had had more experience than with butter. The results he had obtained were more or less in agreement with those now given, except that he usually found a higher insoluble acids figure, and a lower Reichert-Meissl value than the authors had. But he had obtained a Reichert-Meissl figure as high as 9 for cocoanut oil, whereas the highest mentioned by Polenske was 7·7. He had also noticed that, as a rule, the figure for insoluble volatile acids in cocoanut oil was from 2·2 to 2·5 times the Reichert-Meissl value. It was difficult, however, to get samples of cocoanut oil that were perfectly normal. In many cases the " stearine " might

have been removed, and some samples might contain palm kernel oil. It was, perhaps, worth noticing that palm kernel oil gave an average Reichert-Meissl figure of 5, the figure for insoluble volatile acids being 10. As far as the effect of different modes of feeding was concerned, the Polenske numbers seemed to come out very regularly. He did not know whether Polenske had made any notes as to the feeding of the cows in his investigations, but it was a matter of common experience that the use of cake did affect to a certain extent the composition of the butter-fat, and certainly cocoanut cake had some effect in many cases.

Mr. HINKS inquired whether in any of these cases the ordinary Reichert-Wollny figure, as well as the Reichert-Meissl figure, had been determined in conjunction with the Polenske number. If so, it would be interesting to see what difference was made by the use of glycerin and by the more rapid distillation.

Mr. HEHNER said that his experience was quite in agreement with that of the authors, that the relationship between the Polenske number and the Reichert-Wollny number was not in every case so definite that one could safely use it as the basis of a definite charge of adulteration. Broadly speaking, of course, it was agreed that the lower the Reichert-Wollny figure, the lower would be the proportion of insoluble volatile acids. Owing, however, to the varying circumstances under which butter was produced, one could not be guided by broad facts in particular cases. His own experience over some considerable time had been that the Polenske numbers shown by pure butter were about the same as those which the authors had obtained, and it would be seen that the difference between the authors' curve for English butters and Polenske's curve for pure butter-fat would allow a margin of about 10 per cent. for admixture. Then came the question of the state of the insoluble volatile acids. At one time it was thought that fluidity of the insoluble volatile acids indicated the presence of cocoanut oil, and that to a certain extent was true, but it was not universally true. In the case of pure butter showing a low Reichert-Wollny figure the insoluble volatile acids were almost invariably solid. When a low Reichert-Wollny figure was associated with fluid insoluble volatile acids, and especially when the Polenske number exceeded 2, the proof of the presence of cocoanut oil was fairly definite. But in butters showing Reichert-Wollny figures of 25 or over, the insoluble volatile acids were in many cases quite fluid. He did not think it safe to rely upon any single figure, however important it might be in itself. Cocoanut oil, as was well known, had a very low iodine value and a very low refraction, whereas genuine butter with a low Reichert-Wollny figure had almost invariably a high refraction and a high iodine value. In this connection micro-polariscopic examination was of some importance. It was, however, beset by many pitfalls, and used alone would be worth nothing. In the process suggested by Knud Jensen and Kirschner unfortunately the silver caprylate was too soluble, and the solubility too much influenced by temperature and time allowed for the precipitation, to lead to reliable figures.

Mr. ESTCOURT said that, from experiments with butter made in his own laboratory, in connection with some samples that were suspected of containing cocoanut oil, he had come to the conclusion that in genuine butter having Reichert number less than 29 the figure for insoluble volatile acids was rarely over 2.

Mr. HARRISON, in reply, said that it must be agreed that between the figures they

found and those of Polenske there was, as Mr. Hehner had said, an appreciable margin of possible adulteration. Polenske himself stated that nothing under 10 per cent. could be detected that, of course, being the minimum, and each 1 c.c. of increase being taken as equivalent to 10 per cent. of cocoanut oil. Towards the end of the curve, however, there was a wider range of variation still. There was, therefore, considerable difficulty in making the process quantitative, apart from the question of the actual detection of cocoanut oil. If, however, they could satisfy themselves that this process was capable of detecting the presence of cocoanut oil with certainty, it might be possible to arrive at some approximate estimate of the quantity. With regard to saponification, although the authors had only used glycerin, he should think that, as a rule, with alcohol a slightly higher Reichert-Meissl value would be obtained than with glycerin. The difference, however, would not be very great. He knew nothing about the Polenske value under these conditions.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

Proteolysis in Cow's Milk preserved with Formaldehyde. G. Tice and H. C. Sherman. (*Journ. Amer. Chem. Soc.*, 1906, xxviii., 189-194.)—Analyses of samples of milk preserved with formaldehyde show that very considerable proteolysis takes place after some time, the albumin being largely digested before the amount of casein is appreciably reduced, though as digestion proceeds and the casein diminishes the proportion of nitrogen existing as albumin and syntonin changes but little, the increase appearing first in the proteoses, then in the peptones and amino-compounds. Only slightly more nitrogen was precipitated by phosphotungstic acid than by tannin, indicating the presence of only small amounts of diamino-acids. Relatively large amounts of proteoses have been found at a rather advanced stage in the digestion, a result entirely different from that of bacterial digestion of milk. In one case, while 95 per cent. of the casein had been digested, less than 4 per cent. of the original lactose was lost, as compared with milks preserved with sodium fluoride or salicylate or hydrogen peroxide, in which, after 25 to 30 per cent. of the lactose had been destroyed, no marked digestion of the casein was noticed, proving the effect of an added antiseptic in determining the character of the fermentation subsequently undergone. W. H. S.

The Determination of Proteids in Milk. Trillat and Sauton. (*Ann. Chim. anal.*, 1906, vol. 11, pp. 205-207.)—The method is based upon the fact that formaldehyde renders the proteids of milk insoluble. Five c.c. of the milk are diluted to 25 c.c. with water, and the liquid boiled for five minutes, then treated with 5 c.c. of commercial formalin, boiled for two or three minutes longer, and allowed to

,and for five minutes. It is next shaken with 5 c.c. of a 1 per cent. solution of acetic acid and the precipitate collected on a weighed filter, which is washed with water, and subsequently extracted with acetone to remove the fat. Finally, it is dried at 75° to 80° C. and weighed. The following results in grams per litre of milk were thus obtained :

	Proteid.			Proteid.
Cow's milk	39·11	Goat's milk		36·64
Ditto, with 10 per cent. of water	34·33	Ass's milk		21·03
Ditto, with 50 per cent. of water	19·50	Colostral milk (cow)		11·00
Sheep's milk	55·52	Whey		4·50

Experiments are described to show that the proteid is completely separated (the amount of nitrogen in the precipitate is identical with that in the milk), and that the elementary composition of the precipitate agrees with that of casein. The author also concludes that the weight of the proteid is not increased by the action of the formaldehyde, for he finds that casein rendered insoluble by being left under a bell-jar containing traces of trioxymethylene does not alter appreciably in weight, whilst, on the other hand, the strength of a formalin solution is not changed appreciably after precipitating the casein, and the weight of proteid separated from the same milk in different determinations with varying amounts of formaldehyde remains the same. Sterilization of the milk has no influence on the accuracy of the results, and the method is applicable to milk preserved with potassium bichromate.

C. A. M.

On the Use of the "Silver Value" for the Detection of Cocoanut Oil in Butter. F. Jean.

(*Ann. de Chim. anal.*, 1906, vol. 11, pp. 121-124.) The method devised by Wijsman and Reijst (ANALYST, xxxi., 158) has been tried by the author upon twelve samples of doubtful butter, and as the second silver value was invariably lower than the first, the conclusion arrived at was that the butters were abnormal, but free from cocoanut oil. On the other hand, the method of Muntz and Coudon (ANALYST, xxx., 155) gave ratios of 22 to 36, which, in conjunction with the other analytical values, pointed to the presence of cocoanut oil. Thus the following results were obtained with two of the samples :

	Oleo refractometer Reading.	Saponification Value.	Reichert-Meissl Value.	First Silver Value.	Second Silver Value.	Muntz and Coudon's Method.			
						Soluble Acids.	Insoluble Acids.	Ratio × 100.	Polariscope.
Butter, No. 1	35	228	27·2	5·06	4·81	4·81	1·76	36	Abnormal
„ No. 3	35	229	26·2	4·95	4·50	4·50	1·14	26	Abnormal

In order to determine the cause of these contradictory results, the author prepared mixtures of pure butter with 10 per cent. of a cocoanut-oil mixture in

common use for adulterating purposes, and with 10 per cent. of a mixture in equal parts of cocoanut oil, karité, butter, and lard, and obtained the following results :

	Oleo-refractometer Reading.	Saponification Value.	Reichert Meissl Value.	Soluble Volatile Acids.	Insoluble Volatile Acids.	Ratio.	First Silver Value.	Second Silver Value.
Adulterated Butter, No. 1	32·0	220	26·4	4·72	2·29	48	6·18	5·80
,, ,, No. 2	32·5	216	26·7	4·69	1·45	30	6·16	5·52

The presence of the cocoanut oil (3·4 and 2·5 per cent. respectively) is here plainly shown by the ratio in Muntz and Coudon's method, whereas from the silver values both samples would have been judged to be pure. Hence the author concludes that the method of Wijsman and Reijst can only be of value as a confirmative test, and that when it gives negative results cocoanut oil in admixture with other fats may still be present.   C. A. M.

The Characteristics of Karité Butter. F. Jean. (*Ann. de Chim. anal.*, 1906, vol. 11, pp. 201-203.)—Karité or fulwar butter is extracted from the seeds of *Bassia butyracea*, a tree growing in the Himalayas and in the tropical zone of Africa. According to the author, large quantities of the seeds and of the fat are sent to England, the latter being used in the adulteration of butter, lard, and cocoa-butter. The kernels examined by the author had the following composition: Water, 10·05; fat, 35·49; soluble extractives, 26·44; tannin, 3·2; ash, 2·50; and cellulose, 22·52 per cent. The butter is a white, paste-like fat, with a slight odour and an astringent taste. It can be purified by a method similar to that used in deodorizing cocoanut oil for food purposes. The following analytical values were obtained with a sample of the fat extracted with petroleum spirit and of fat prepared by the natives by crushing the nuts with water:

Fat.	Oleorefractometer at 45 C.	Melting-point.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Soluble Fatty Acids.	Hehner Value.
Extracted in laboratory	+22°	°C. 30	—	175–176	—	2·6	—	—
As imported	+18°	30	9	175	19·75	1·19	trace	91·2

The fat consisted of 69·28 per cent. of solid fatty acids, 21·92 per cent. of liquid acids, and 8·85 per cent. of glycerin. The fatty acids, separated by Renard's method, melted at 67·8° C. Neither caproic nor caprylic acid was present in the butter.   C. A. M.

The Action of Flour, etc., on Hydrogen Peroxide. W. Bremer. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, xi., 569-577.)—The author's experiments show that the method proposed by Wender (ANALYST, 1906, xxxi., 73) for the valuation of

dours is at present of little use. The evolution of oxygen is erratic, equal weights of the same flour yielding varying volumes of gas, and the quantity is not proportional to the amount of flour employed, or to the percentage of bran in the flour. The power of decomposing hydrogen peroxide is diminished if the flour be heated previously to a temperature of 98° C., a moist heat having more effect than a dry heat. As both the aqueous extract and the insoluble residue, obtained on extracting bran with water, decompose hydrogen peroxide, the assumption is raised that more than one constituent of the bran is capable of causing the decomposition. The presence of mercuric chloride or of hydrochloric acid inhibits the reaction, as does also that of alcohol. Whilst well-washed gluten decomposes hydrogen peroxide to a slight extent, no action was noticed in the case of aqueous solutions of diastase.

W. P. S.

Formic Acid as a Preservative of Lemon-Juice. Von Küttner and Ulrich. (*Zeit. öffentl. Chem.*, 1906, xii., 201-207.)—The deterioration of fresh lemon-juice due to the formation of acetic acid may be prevented by the addition of from 0·1 to 0·4 per cent. of formic acid. The addition, of course, increases the acidity of the juice, and the results of experiments are given which show that the formic acid distils over quantitatively with the other volatile acids present in the juice.

W. P. S.

Composition of Tomatoes and Tomato-Juice. W. Stüber. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, xi., 578-581.)—The following results were obtained on the analysis of two samples of tomatoes and their respective juices:

	Fruit, 1.	Fruit, 2.	Juice, 1.	Juice, 2.	Juice, 3.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Water	94·52	95·13	96·00	96·19	95·48
Nitrogen	0·116	0·159	0·098	0·088	0·128
Ash	0·50	0·63	0·50	0·63	0·65
Alkalinity of ash (c.c. ½ acid) ...	4·62	5·50	5·20	6·00	6·40
Petroleum spirit extract ...	0·06	0·07	—	—	—
Sugars (after inversion)	2·51	3·21	2·34	1·96	2·53
Free acid (as citric)	0·41	0·48	0·60	0·61	0·46
Phosphoric acid (P_2O_5)	0·044	0·059	0·031	0·039	0·025

The sample of juice No. 3 was obtained from Canadian tomatoes, the other samples being of German origin. Tartaric, malic, and succinic acids could not be detected in any of the samples.

W. P. S.

Determination of Talc on Rice, Pearl-Barley, etc. R. Kržižan. (*Zeit. Untersuch. Nahr. Genussm.*, 1906, xi., 641-650.)—The quantity of talc present as a coating on rice, pearl-barley, or other grain can only be correctly determined by directly weighing the mineral after detaching it from the grains. As the mineral is

readily attacked by hydrochloric acid, especially after ignition, the method proposed by Matthes and Müller (ANALYST, 1905, xxx., 206) is untrustworthy, and methods based on the determination of the magnesia in the ash of the sample (the magnesia being subsequently calculated into talc) give incorrect results, owing to the varying composition of the mineral itself, and to the magnesia natural to the grains. The author, therefore, employs a process in which a weighed portion of the sample is heated with a little hydrogen peroxide and dilute ammonia; bubbles of gas form between the grain and its coating, and completely loosen and remove the latter. The turbid liquid is decanted, the grains are shaken and washed several times with water, and the total liquid then rendered acid with hydrochloric acid, and the organic matter oxidized by the addition of a few grams of chromic acid. The mixture is heated to boiling, filtered, and the residue is washed with water and ignited at the lowest possible temperature. The weight of residue obtained represents the amount of talc in the portion of the sample taken. Besides talc, other minerals, such as mica and certain clays, are used for coating grains. (*Cf.* " Facing of Rice," this vol., p. 40.)   W. P. S.

The Determination of Alcohol in Chloroform. M. Nicloux. (*Bull. Soc. Chim.*, 1906, xxxv., 330-335.)—A small proportion of alcohol is commonly added to chloroform as a preservative. It can be separated by shaking 5 c.c. of the sample with 20 c.c. of water, which extracts the whole of it, and it can then be determined in the supernatant aqueous layers by the author's bichromate method. Five c.c. of this alcoholic solution (containing not more than 1 part of alcohol in 500) are mixed in a test tube with 0·1 to 0·2 c.c. of a solution of potassium bichromate (19 grams per litre), and then with pure sulphuric acid (66° B.), which, when added in sufficient quantity (4·5 to 6 c.c.) decolorizes the solution. The liquid is now gradually titrated with the bichromate solution, being shaken and gently heated after every addition, until the colour changes from greenish-blue to a permanent greenish-yellow. The change is most readily recognised in solutions containing less than 0·2 per cent. of alcohol. It is advisable to make a second determination in which the amount of bichromate used in the first experiment, less 0·1 c.c., is run in at once, the sulphuric acid added, and the liquid boiled for a moment. The contents of the tube ought to remain greenish-blue, whilst in another determination in which 0·1 c.c. more than the first reading is added, the colour should change to greenish-yellow. The number of c.c. consumed, divided by 1,000, gives the amount of absolute alcohol in c.c. per c.c. of solution. When the proportion of alcohol is less than 0·1 per cent. it is best to double the strength of the bichromate solution. Six samples of chloroform examined by this method were found to contain from 1·4 to 10·4 c.c. of absolute alcohol per litre. Test experiments with chloroform containing known quantities of alcohol showed that the results were concordant and accurate.

                                                                    C. A. M.

TOXICOLOGICAL ANALYSIS.

A Colorimetric Method of Determining Morphine. L. Georges. (*Journ. Pharm. Chim.*, 1906, **xxiii.**, 513-516.)—The solution of morphine, extracted by the Stas-Otto method, gives a yellow or yellowish-red coloration on treatment with iodic acid, and the colour changes to yellowish-brown on the addition of ammonia. In each case the intensity of the colour is proportional to the amount of morphine, and can be matched with the shade produced by a standard solution of morphine 1·256 grams of morphine hydrochloride per litre. 0·001 gram of morphine per c.c.). In making a determination, 5, 10, or 20 c.c. of the solution of unknown strength and the same quantity of the standard alkaloid solution are treated simultaneously with 5 c.c. of a 5 per cent. solution of iodic acid, and the colours compared, before and after the addition of 5 c.c. of a 10 per cent. solution of ammonia. The colour produced by the iodic acid alone reaches its maximum intensity after half a minute, and begins to fade after fifteen minutes. In the case of the ammoniacal coloration the maximum is only reached after two or three minutes. The author states that this method has invariably yielded good results in his hands, but points out that the reduction of iodic acid cannot be regarded as an absolute test of the identity of morphine extracted by Stas's method.　　　　　　　　　　　　C. A. M.

On the Quantitative Toxic Properties of Carbolic Acid as compared with those of other Poisons. Th. Bokorny. (*Chem. Ztg.*, 1906, **xxx.**, 554.) The author points out that in order to estimate correctly the toxic properties of any substance, it is necessary to ascertain not only the degree of dilution at which it will still act, but also the total minimum quantity necessary, and complains that this fact is commonly lost sight of in the case of antiseptics. He has determined the "lethal dose" for a number of poisons acting on 10 grams of fresh brewers' yeast (containing 30 per cent. of dry substance), and communicates his results, together with some previously published, as follows: Carbolic acid, between 0·05 and 0·1 gram; formaldehyde, 0·02 to 0·04; acetaldehyde, above 0·5; o-oxybenzaldehyde, 0·25 to 0·5; acetic acid, 0·2 to 0·4; copper sulphate, 0·001 to 0·0025; corrosive sublimate, 0·005 to 0·01; sodium fluoride, 0·05 to 0·1; hydrofluoric acid, 0·01 to 0·025; silver nitrate, 0·01 to 0·02; zinc sulphate, 0·05 to 0·1; lead acetate, 0·05 to 0·1; hydrochloric acid, 0·05 to 0·1; caustic soda, 0·05 to 0·1; potassium permanganate, 0·02 to 0·05; chlorine, 0·015 to 0·03; tannic acid, 0·5 to 1.　　　A. G. L.

ORGANIC ANALYSIS.

Analysis of Sugar Mixtures. C. A. Browne. (*Journ. Amer. Chem. Soc.*, 1906, **xxviii.**, 439-453.)—Since the weights of two different sugars reducing the same amount of copper bear a constant ratio to one another, the differences in the reducing powers of the various sugars can be very simply expressed by determining this ratio for each sugar, compared with dextrose as a standard. These constants are termed the "dextrose ratios" or "equivalents," and based on the conclusions that (1) the

dextrose equivalent of a mixture of reducing sugars is equal to the sum of the dextrose equivalents of the individual sugars (which the author has proved, notwithstanding statements to the contrary); and (2) the polarization of a mixture of sugars is equal to the sum of the polarizations of the individual sugars present, formulæ are developed which enable the percentage composition of a mixture of any two sugars, or of three sugars, one of which is sucrose, to be ascertained from determinations of the copper-reducing power of the mixture and of its polarization. Two sources of error arise in such separations, due to (1) the slight reducing action of sucrose upon Fehling's solution, and (2) the change in rotation of lævulose in neutral and acid solution. In some experiments with a mixture of dextrose and sucrose, the error due to the first-mentioned cause is found to be inversely proportional to the amount of dextrose present, and the following correction gives concordant results: Divide the grams of sucrose in the 25 c.c. of solution to be analysed by Allihn's method by the mgms. of dextrose found +40, and subtract the quotient in grams from the dextrose found. The correction for the second source of error depends upon the concentration of the acid used for inversion and the dilution of the sugar solution; for 10 c.c. fuming HCl (specific gravity 1·18) and 100 c.c. of sugar solution the correction is 0·036 per cent. for each percentage of lævulose. Experiments on a number of known mixtures of various sugars have proved the accuracy of the method.   W. H. S.

On the Colour Reactions of Sesame Oil. P. Soltsien. (*Chem. Rev. Fett. u. Harz-Ind.*, 1906, xiii., 138.) — Further experiments have confirmed the author's conclusion that the furfural reaction and the tin reaction of sesame oil are not due to one and the same substance. Both compounds can be extracted by shaking the oil with alcohol of 90 per cent. strength, but thorough extraction with hydrochloric acid of specific gravity 1·125 removes the substance that gives the furfural reaction, whilst the oil still gives the tin reaction as strongly as before. The tin reaction is also quite independent of Bishop's reaction. Hence, if a sesame oil for any reason gives neither the furfural nor Bishop's reaction, it may still be possible to identify it by the tin reaction (see ANALYST, xxvii., 363; xxviii., 298, 364).

                                                    C. A. M.

On Indian Ghedda Wax. Georg Buchrer. (*Chem. Zeit.*, 1906, xxx., 525.) —The author takes exception to the statement of Dr. J. König (" Die Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe," ed. 1906, p. 939), that the Ghedda wax of India is not to be regarded as real beeswax. The matter is of importance, since for church use only candles made from beeswax may be used. Ghedda wax is produced by three species of bees, two of which—*Apis dorsata* and *Apis florea*—stand evolutionally directly before the European *Apis mellifica*, whilst the third—*Apis indica* or *fasciata*—appears to be a variety of *Apis mellifica*. Ghedda wax is qualitatively of the same composition as ordinary beeswax, but differs from it quantitatively, the amount of free cerotic acid being very much less and the

quantity of esters very much higher in the Indian wax. This is shown in the following table :

Source.		Melting-point, 0° C.	Acid Number.	Saponification Value.	Iodine Value (Hubl).
Apis dorsata ... (23 samples)	Average	63·1	7·0	96·2	6·7
	Maximum	67·0	10·2	105·0	9·9
	Minimum	60·0	4·4	75·6	4·8
Apis florea ... (5 samples) ...	Average	61·2	7·5	103·2	8·0
	Maximum	68·0	8·9	130·5	11·4
	Minimum	63·0	6·1	88·5	6·6
Apis indica ... (7 samples)	Average	63·25	6·8	96·2	7·4
	Maximum	64·0	8·8	102·5	9·2
	Minimum	62·0	5·0	90·0	5·3
Apis mellifica ...	Average	63·25	20·0	95·0	7·5
	Maximum	65·0	21·0	99·0	11·0
	Minimum	61·5	17·50	87·5	4·0

The author is of opinion that Ghedda wax is to be regarded as a true beeswax, and as such admissible for church use.   A. G. L.

The Reaction of Mercuric Acetate with Camphene and Pinene. L. Balbiano. (*Reale Accad. di Lincei;* through *Pharm. Journ.,* 1906, vol. 76, p. 611.)—When equal volumes of benzene and an essential oil containing camphene are shaken with a 25 per cent. solution of mercuric acetate, and allowed to stand for thirty days, a crystalline compound, $C_{10}H_{16}O(HgC_2H_3O_2)_2$, is formed which is insoluble in water, alcohol, and ether. When the crystals are suspended in water and treated with a current of hydrogen sulphide they regenerate camphene. When pinene is subjected to prolonged contact with aqueous mercuric acetate solution, the reaction is quite different, Δ^6 oxymenthenone being formed.   W. P. S.

A New Method for the Determination of Nitrogen in Nitrocellulose. M. Busch. (*Chem. Ztg.,* 1906, xxx., 596.)—The nitrocellulose is saponified with caustic alkali in the presence of hydrogen peroxide, which prevents reduction of the nitrate by the cellulose further than to nitrite. On acidifying in the presence of hydrogen peroxide, the nitrite is also quantitatively oxidized to nitrate. The determination is then completed by adding "nitron," and weighing the nitron nitrate ($C_{20}H_{16}N_4 \cdot HNO_3$).   A. G. L.

Extraction of Tanning Materials for Analysis. F. P. Veitch and H. H. Hurt. (*Journ. Amer. Chem. Soc.,* 1906, xxviii., 505-512.)—Further experiments with the continuous extractor confirm the conclusion that this extractor gives the most complete extraction, all soluble constituents being removed by it in larger quantities than by other extractors. It has been stated that with sumac and canaigre

the temperature must be kept at from 50° to 60° C. until at least half the volume of the extract is obtained ; but these materials were extracted satisfactorily in the continuous extractor with from 200 to 300 c.c. of water below 100° C., the extraction being completed at steam heat. All materials should be ground to pass at most a millimetre sieve, and extraction should be continued for at least sixteen hours, preferably for twenty-four hours.   W. H. S.

Strychnine Tannate and its Application to the Analysis of Tanning Materials. S. R. Trotman and J. E. Hackford. (*Ledermarkt, Collegium*, 1906, 69 ; through *Chem. Zeit.*, 1906, xxx., *Rep.* 167.)—The tannate of strychnine is almost insoluble in water, whilst the gallic acid compound is easily soluble. In making an analysis, the tanning material is extracted with alcohol. The extract, which should contain about 0·5 gram of active substance, is evaporated to 50 c.c., and made up to 100 c.c. with water. The liquid is filtered from the resinous bodies, and 25 c.c. of the filtrate are diluted with water, after which 0·25 gram of strychnine dissolved in 50 c.c. of alcohol and 50 c.c. of water is added, and the whole diluted to 250 c.c. with water. The precipitate is filtered off on to a Gooch crucible and dried in vacuo. Experiments with pure tannin showed that if an excess of strychnine is present, the tannate contains 1 molecule of strychnine for every 1 molecule of tannic acid.   A. G. L.

The Determination of Uric Acid in Urine. G. Guérin. (*Journ. Pharm. Chim.*, 1906, xxiii., 516, 517.)—One gram of anhydrous sodium carbonate is dissolved in 120 to 125 of the urine and the resulting precipitate of phosphates separated by filtration. One hundred c.c. of the filtrate are mixed with 25 c.c. of a solution of ammonium nitrate (50 grams in 100 c.c.), followed by 5 c.c. of ammonia solution, and allowed to stand until the next day, when the uric acid will have been quantitatively precipitated as ammonium urate. The precipitate is collected, washed with a solution containing 10 per cent. of ammonium nitrate and 1 per cent. of ammonia, and transferred with the aid of a jet of water into an Erlenmeyer flask. The turbid liquid (about 100 c.c. is mixed with 40 c.c. of sulphuric acid (1 : 1), heated to 50° C., and titrated with a standard solution of potassium permanganate (1·5 gram per litre), the flask being shaken after each addition. The number of c.c. consumed multiplied by 0·00350 gives the amount of uric acid in 100 c.c. of the urine. The method is directly applicable to urines containing albumin. Urines that give a deposit of urate ought to be slightly heated on the water-bath and shaken until the sediment dissolves, before the addition of the sodium carbonate.   C. A. M.

Estimation of Ammonia in Used Lime Liquors. H. R. Procter and D. McCandlish. (*Journ. Soc. Chem. Ind.*, 1906, xxv., 254-256.)—A current of air, freed from carbon dioxide and ammonia by passage through U-tubes filled with NaOH and H_2SO_4, is rapidly drawn, by means of a water-pump, through the ammoniacal liquor contained in a " glass worm " immersed in a water-bath at 90° C., and thence through a U-tube containing a known volume of standard acid. Frothing is obviated, and the time required reduced from one hour to thirty minutes by

replacing the " glass worm " by the following apparatus : A piece of glass tubing, A ,about $\frac{3}{16}$-inch bore), is drawn out to a fine point at one end, which is bent up as shown in the figure. Over this point is fixed, by wiring round a piece of cork, a second tube, B, of the same diameter as A, but slightly widened at the end. The tubes are then fitted in a wide test-tube (10 inches by 2 inches) containing sufficient water to cover their junction, the long arm of A passing through a two-holed rubber stopper,
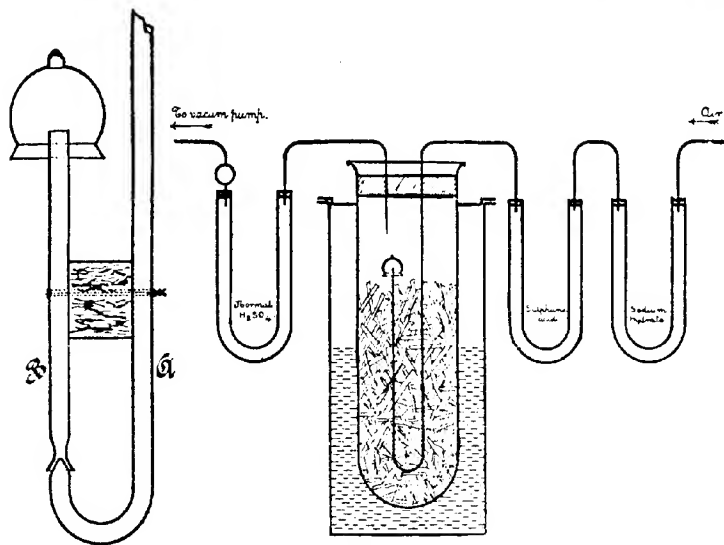

FIG. 1.

and being connected with U-tubes containing NaOH and H_2SO_4 for purifying the air. Through the other hole of the stopper is a short piece of bent glass tubing making connection with a U-tube containing 30 to 40 c.c. of $\frac{N}{10}$ acid, which in turn is attached to the pump. The tubes A and B are so adjusted that the passage of the air causes a continuous stream of water up to B, air also escaping from the bottom of B and rising outside it. The test-tube is filled with broken glass up to within 2 inches of its top, and over the end of B is placed the inverted head of a thistle funnel, the aperture where the stem was connected having been carefully sealed. The tube is then placed in a water-bath at 90° C., 50 c.c. of the lime liquor introduced into A through a filter funnel, and slight suction applied, whereby the liquor is continuously raised to the top of B and thrown back by the thistle funnel upon the broken glass, whence it runs back to the bottom of the tube, the ammonia being thus completely drawn off within thirty minutes. W. H. S.

Notes on the Determination of Ash in Elementary Organic Analysis.

Fritz von Konek. (*Chem. Ztg.*, 1906, xxx., 567.)—The author finds that in

analysing coals the amount of ash left in the carbon and hydrogen determination (carried out in an electrically-heated furnace) is always higher than that given by the usual method of ashing the sample in a platinum crucible in the air. He shows that platinum boats increase in weight (up to 0·8 mgm.) on ignition in oxygen, coming back to their original weight on prolonged heating in air. Many substances (calcium carbonate, iron oxides, etc.) also behave differently according as to whether ignited in oxygen or air. Finally, the quantity taken for the elementary analysis is so small that it is very difficult to obtain a fair sample as regards ash. For all these reasons, the author prefers to take the usual ash figure obtained by burning 1 or 2 grams of the fuel in a crucible. A. G. L.

Combustion of Halogen Compounds in Presence of Copper Oxide. C. J. Robinson. (*Amer. Chem. Journ.*, 1906, vol. 35, pp. 531-533.)—The need for a separate combustion tube filled with lead chromate is obviated by placing just in front of the boat in the ordinary combustion tube a cartridge of heavy copper wire gauze rolled into the form of a hollow cylinder, 6 or 7 cm. long, and filled with pure lead chromate, the ends being closed by wrapping with Cu wire, which, passing also lengthwise through the cartridge, is looped at each end to facilitate removal from the tube. The arrangement has given good results for the determination of C, H, and N in halogen compounds, and would probably also be suitable for the estimation of C and H in sulphur compounds. W. H. S.

INORGANIC ANALYSIS.

Sampling of Gold Alloys. E. A. Smith. (*Chem. News*, 1906, 93, pp. 225, 226.) Analyses are given proving the importance of carefully removing the coloured surface from gold alloys of all standards before taking the sample for assay, whether by cutting or scraping, the error due to inclusion of the coloured surface amounting with cut samples to as much as 1·27 per cent., and with scraped samples to 13·57 per cent. W. H. S.

The Detection of Gold and Platinum in Inorganic Analysis. J. Petersen. (*Zeit. anal. Chem.*, 1906, xliv., 342-344.)—The solution of the metals, which should be slightly acid, is treated with an excess of zinc turnings, which precipitate mercury, silver, lead, bismuth, copper, cadmium, platinum, gold, arsenic (part escapes as arseniuretted hydrogen), antimony, and tin, with some cobalt and nickel, in a granular or spongy form. The contents of the vessel are gently heated for about fifteen minutes and filtered, and the filtrate examined as in the case of the usual filtrate from the hydrogen sulphide precipitation. The precipitate is washed and heated with dilute hydrochloric acid, which dissolves the excess of zinc, the cadmium and tin, and some cobalt. The residue is washed until the washings give no reaction with silver nitrate, and is then boiled with dilute nitric acid. This dissolves the mercury, lead, copper, bismuth, and nickel, leaving a residue of gold, platinum, antimony, and antimonic acid. This residue is washed, dried, and ignited in a porcelain crucible with 1 to 2 parts of ammonium nitrate, and 5 parts of ammonium

chloride, with the result that the antimony is volatilized as chloride, and a residue of unaltered gold and platinum obtained. They are dissolved in *aqua regia* and the solution divided into two parts, one of which is tested for platinum by means of ammonium chloride, and the other for gold by means of sulphurous acid or an alkaline solution of hydrogen peroxide. The filtrates are united, and after evaporation of the free acid, the other metals are precipitated by means of hydrogen sulphide. It is stated that platinum and gold were readily detected by this method in 50 c.c. of a solution containing 0·04 per cent. of the former and 0·01 per cent. of the latter, with about 0·5 per cent. of each of the other metals. C. A. M.

The Action of Sulphuric Acid on Platinum. M. Quennessen. (*Chem. News*, 1906, vol. 93, p. 271.)—It was asserted by Scheurer-Kestner that the solution of platinum in sulphuric acid was accelerated by the presence of nitrous products; but this was denied by Conroy (*Journ. Soc. Chem. Ind.*, xxii., 465), and Delépine (*Comptes Rendus*, 1905, 866, 1013) found that the addition of nitric acid had no influence on the speed of solution. The author's experiments have been made with commercial and pure platinum and sulphuric acids of 94 per cent. strength upwards, the heating being done both *in vacuo* and in an atmosphere of oxygen. In the case of commercial platinum and 94 per cent. acid, 0·001 gram per square decimetre of metal was dissolved in an hour *in vacuo*, whilst 0·124 gram was dissolved in oxygen. With sulphuric acid containing 2 per cent. excess of anhydride pure platinum was dissolved *in vacuo* to the extent of 0·0265 gram per square decimetre per hour, and sulphurous acid could be detected on opening the tube. The author concludes from these and other experiments that in the case of acid of the ordinary commercial strength it is atmospheric oxygen that acts as the oxidizing agent, whilst with acids of greater concentration the oxygen required is, in the absence of atmospheric oxygen, supplied by the sulphuric anhydride contained in solution in the sulphuric acid. C. A. M.

A New Reaction of Nickel. C. Reichard. (*Chem. Ztg.*, 1906, xxx., 556.)— If anhydrous nickel sulphate is intimately mixed with an equal quantity of methylamine hydrochloride ($CH_3NH_2.HCl$), and the mixture heated in a small porcelain crucible until white fumes are given off, a blue colour is developed, which is very delicate at first, but increases in intensity with the heating. On removing the source of heat, the colour is almost immediately changed back to that of the yellow nickel sulphate, but renewed heating will reproduce the blue colour as long as any methylamine hydrochloride is left. As little as 0·0001 gram of nickel will give a decided blue colour. The nitrate and chloride behave in the same way. If cobalt nitrate is heated, on the other hand, a blue colour is obtained whether methylamine hydrochloride is present or not, and this colour is not changed by interrupting the heating. The disappearing of the blue colour consequently appears to be characteristic of nickel. A. G. L.

A New Reaction of Tin. C. Reichard. (*Pharm. Centralh.*, 1906, vol. 47, p. 391; through *Chem. Ztg.*, 1906, xxx., *Rep.*, 177.)—Any stannic compound—*e.g.*, stannic chloride—treated with caustic soda and then warmed with finely powdered

uric acid in a porcelain crucible, yields a gray to intensely black stain. The reaction is not given by stannous compounds, arsenic, antimony, mercury, copper, lead, bismuth, or cadmium.   A. G. L.

The Determination of Cadmium. C. Goldschmidt. *(Zeit. anal. Chem.,* 1906, xliv., 344.)—Cadmium is quantitatively precipitated when a solution of one of its salts is boiled in an aluminium vessel in the presence of a trace of chromium nitrate and cobalt nitrate. The precipitation is as complete as that of gold by nickel or of silver by cobalt, and is also successful in the presence of other metals.

                                                           C. A. M.

Complete Analysis of Ferrochrome. G. Dillner. *(Jernkontorets Annaler,* 1906, vol. 60, p. 253; through *Chem Zeit.,* 1906, xxx., 178.)—Carbon is determined by combustion with lead peroxide in a current of oxygen. For chromium the sample is heated with sodium peroxide in a nickel crucible; the melt is taken up in boiling water, and chromium titrated with ferrous sulphate in the filtered and acidified solution. Iron is determined by titration in the insoluble residue from the melt, manganese being determined by Volhard's method in another similar residue. For silicon the sample is fused with sodium peroxide, and the melt obtained dissolved in hydrochloric acid; the solution is reduced with alcohol, chromium and iron hydroxides precipitated by ammonia, dissolved in hydrochloric acid, this solution evaporated to dryness, and silica determined as usual. In the filtrate phosphorus is determined. For sulphur another portion is fused with sodium peroxide.   A. G. L.

The Detection and Determination of Traces of Iron. A. Mouneyrat. *(Comptes Rendus,* 1906, cxlii., 1049-1051.)—On treating 50 c.c. of the very dilute solution of the iron salt with 3 c.c. of ammonia solution (62 grams of NH_3 per litre) and passing a current of hydrogen sulphide for ten to twelve minutes, a dark green coloration is obtained, the iron apparently being present in a colloidal state. The test is very sensitive, and is capable of detecting 1 part of iron in 800,000. The green colour is destroyed by mineral acids and by many inorganic salts, such as sodium sulphate or chloride in concentrated solution. On the other hand, many organic substances increase the stability of the colloidal condition—*e.g.,* glycerin, glucose, mannite, as well as lactic, tartaric and citric acids, whilst albumin has a particularly marked effect in rendering the reaction more sensitive (1 in 1,000,000). Mercury, lead, silver, chromium, nickel, cobalt, copper, and metals of the alkaline earths, do not give any coloration. Copper, however, interferes with the test for iron, and should be removed by means of hydrogen sulphide. The intensity of the green coloration is proportional to the amount of iron for solutions containing 1 part in 1,000 to 1 in 1,000,000, and a colorimetric determination may be made with the aid of standard solutions of iron.   C. A. M.

Modified Evolution Method for the Determination of Sulphur in Pig-Iron. J. McFarlane and A. W. Gregory. *(Chem. News,* 1906, vol. 93, p. 201.)— The powdered pig-iron is heated to redness with cream of tartar, and the hydrogen

sulphide liberated by treating the mixture with hydrochloric acid titrated with standard iodine solution. Five grams of the powdered sample are intimately mixed with about 0·5 gram of cream of tartar, the mixture wrapped in filter-paper, placed in a small covered crucible, and heated to bright redness in a muffle for a quarter of an hour. After cooling, the resulting mass is powdered in a glass mortar and transferred to the evolution flask, where it is treated with boiling HCl (2 parts acid to 1 part water), the delivery tube from the flask dipping into an ammoniacal solution of cadmium chloride, prepared by dissolving 20 grams of the latter in a litre of water and adding a litre of strong ammonia. For each estimation 25 c.c. of this solution is diluted with about 300 c.c. of water, and placed in a tall beaker. The last traces of hydrogen sulphide are expelled from the flask by boiling, and the liquid containing the cadmium sulphide in suspension is acidified with hydrochloric acid, and the hydrogen sulphide in solution immediately titrated with standard iodine solution, each c.c. of which is equivalent to 0·00025 gram of sulphur, and standardized by means of a steel of known sulphur content. The cream of tartar should be free from sulphur. Results obtained by this process are found to agree very approximately with those found by the " aqua regia " method. W. H. S.

The Determination of Potassium in Potassium Salts and Artificial Manures. M. Kling and O. Engels. (*Zeit. anal. Chem.*, 1906, xlv., 315-332.) — The following simpler modification of the Finkener-Neubauer method is recommended : 10 grams of the potassium salt are dissolved in 500 c.c. of water, and 25 c.c. of the solution (= 0·5 gram) mixed with a few drops of hydrochloric acid and the required amount of platinum chloride, and evaporated to dryness in a porcelain basin. The residue is taken up with water and alcohol as in Neubauer's method, collected in a Neubauer-Gooch crucible, washed with alcohol, and dried by placing the crucible on a moderately hot metal plate. It is next reduced in a current of coal-gas, the heating being done with a very low flame for the first ten minutes, and finally at a faint red heat for twenty minutes. When the reduction is complete, the crucible is heated for two minutes over the naked flame of a Teclu burner, and, after its contents have been washed about fifteen times with hot water and two or three times with cold 15 per cent. nitric acid, it is placed in a porcelain vessel containing nitric acid, of the same strength, the level of liquid reaching to about three-quarters of the height of the crucible. The vessel is covered with a clock-glass, heated for thirty minutes on the boiling water-bath, and allowed to cool. Finally, the platinum in the crucible is washed with hot water and alcohol, ignited, and weighed, and the weight calculated into the corresponding amount of potassium. The accuracy of the method is shown by the results of test analyses of different potassium salts.

In the case of artificial manures, 20 grams of the sample are shaken with about 500 c.c. of water for thirty minutes in a litre flask, the liquid then made up to the mark and filtered, and the potassium determined in the filtrate. For the potassium 100 c.c. (= 2 grams) are treated with ammonia and ammonium carbonate in a 200 c.c. flask, the mixture made up to 200 c.c. and filtered, and 50 c.c. (= 0·5 gram) evaporated in a platinum basin. The residue is dried, and, after volatilization of the ammonium salts, ignited until it begins to fuse, and then taken up with hot

water and a little hydrochloric acid. As a rule, solution is complete, but occa-
sionally there is a residue, which must be filtered off. The liquid is treated with
platinum chloride solution (2 c.c. of a 10 per cent. solution is usually sufficient)
and evaporated to dryness, and the potassium determined as above described. It
is shown that the presence of phosphates does not interfere with the accuracy of the
results. The paper concludes with a table for calculating the amount of potassium
(as K_2O) from the weight of platinum obtained from 0·5 gram of the substance.
(Factor 0·48108.)   C. A. M.

Determination of Sulphur in Pyrites. C. R. Gyzander. (*Chem. News*,
1906, 93, pp. 213, 214.)—The sulphur is precipitated as $BaSO_4$ after reducing the
iron to the ferrous state by hydroxylamine hydrochlorate. About 0·2 gram of the
finely powdered ore is heated with a mixture of 5 c.c. concentrated HCl, and 15 c.c.
concentrated HNO_3, evaporated to dryness, another 5 c.c. concentrated HCl added,
and again evaporated. To the residue is added 100 c.c. distilled water, 1 c.c. con-
centrated HCl, and 3 c.c. hydroxylamine hydrochlorate solution, containing 1 ounce
of the salt in 500 c.c. water, and when reduction is complete the solution is filtered,
the filtrate heated almost to boiling, and 10 c.c. of a cold 10 per cent. $BaCl_2$ solution
added. The $BaSO_4$ is then filtered off, washed, dried, and weighed.   W. H. S.

Determination of Phosphorus and Ash in Coke. J. F. Hoy. (*Foundry*,
1906, vol. 28, p. 155; through *Chem. Ztg.*, 1906, xxx., *Rep.*, 178.)—To determine
ash, 1 gram of the finely-powdered coke is mixed to a thin paste with absolute
alcohol in a platinum dish of 150 c.c. capacity; the dish is rotated slowly, so as to
distribute the mixture uniformly over the whole of the inside, and the motion
continued until the alcohol has evaporated. From five to seven minutes' heating
over a blast-lamp or in a muffle is then sufficient to completely ash the coke. To
determine phosphorus, the ash obtained as above is treated with 10 c.c. dilute
hydrochloric acid and 29 (? 20) c.c. hydrofluoric acid, and the whole evaporated to
dryness. The residue is taken up in 15 c.c. hydrochloric acid; the solution is trans-
ferred to a flask, and treated with ammonia, nitric acid, and molybdic acid, the
determination then being finished as usual.   A. G. L.

**Chemical Methods for the Examination of Coal Briquettes and Bri-
quette Pitch. E. J. Constam and R. Rougeot.** (*Glückauf*, 1906, vol. 42,
p. 481; through *Chem. Ztg.*, 1906, xxx., *Rep.*, 178.)—Briquettes should be made
from hard coal, but not anthracite, and should contain a certain amount of binding
material. The coal used, and the briquettes themselves, should be examined for
coke yielded on carbonizing. In Germany, Austria, and Switzerland, Muck's method
is used for this purpose. Broockmann's "Bochum" test gives results 1 to 3 per
cent. lower, but in good accord with the results obtained in gasworks. The Belgian
method gives variable results. The American method gives the best results. It
consists in heating 1 gram of the undried coal in a covered platinum crucible weigh-
ing 20 to 30 grams in a Bunsen flame 20 cm. high, at a point 6 to 8 cm. above the
burner. To determine the coke yielded by the pitch used in making briquettes, the

Bochum method is to be preferred. The amount should not exceed 45 per cent. The softening and melting points of the pitch should be noted, and also its behaviour in the molten state. The amount soluble in carbon bisulphide varies from 60·4 to 95 per cent., the average being 79·8 per cent. The calorific value of the pitch should not be below 8,550, and the quantity of hydrogen present should not exceed 5 per cent.

To determine the amount of binding material in the briquettes, the sample should be twice extracted with carbon bisulphide in a Soxhlet for twenty-four hours at a time, the extract being dried for three days over phosphorous pentoxide *in vacuo*. The amount obtained should not be less than 5 per cent. The ultimate composition of the briquettes should also be determined. The calorific value of the dry briquette should not be less than 7,700, the ash not more than 8 per cent., and the amount of volatile matter not less than 16 per cent.   A. G. L.

On the Determination of Water-soluble and Total Phosphoric Acid in Superphosphate. K. Rohm. *(Chem. Zeit.,* 1906, xxx., 542.)— *Water-soluble Phosphoric Acid.*—A number of determinations were made on three samples to compare the method in which the sample is digested with water for two hours, with occasional shaking, with that in which it is agitated continuously with water for thirty minutes in a shaking machine, different speeds being also tested. The most constant results are given by the latter method, the speed being about thirty to forty rotations per minute, but digesting the sample without any shaking at all gave results only about 0·2 per cent. too low (with 19 per cent. of water-soluble P_2O_5). The sample used should pass through a 2 mm. mesh sieve.

Total Phosphoric Acid.—Extraction with nitric acid, with a mixture of nitric and sulphuric acids, and with aqua regia, gave practically identical results. Extraction with hydrochloric acid, which is never used in practice, gave results about 0·2 per cent. too low. The magnesia precipitate should be allowed to stand twenty-four hours before filtering, or else mechanically stirred for thirty minutes. On allowing it to stand for only two hours, an error of up to 0·22 per cent. of P_2O_5 was found in a number of analyses.   A. G. L.
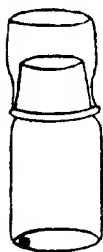
On the Determination of Nitric Acid in Water. Paul Drawe. *(Chem. Zeit.,* 1906, xxx., 530.)—The author has altered Frerich's method *(Arch. d. Pharm.,* 1903, 241, 47) as follows : If nitrates have been qualitatively shown to be present, 100 c.c. of the water are evaporated to dryness with an excess of hydrochloric acid. The residue is evaporated several times with water, until every trace of free acid is removed, after which the chlorine in the residue is determined by titration. From the value found the chlorine present in the water itself, plus that due to the alkalinity of the original water, is deducted, and the remainder calculated to nitric acid. The method is said to give good and accurate results.   A. G. L.

APPARATUS.

A New Weighing-Bottle.—This improved form has many decided advantages over those in use, being easier and more cleanly to work with, and insures greater accuracy in weighing. Also, it may be used for purposes for which the old form was not adapted. The old form has the stopper ground to fit inside the neck; the new one has the stopper ground to fit like a cap over the neck of the bottle. The advantages claimed are: (1) On tipping out many substances from the old form of bottle, some remains sticking to its lip, and is left exposed to the air when the stopper is replaced, thus absorbing moisture. With the improved stopper the lip remains enclosed, and any substance adhering to it cannot absorb moisture from the air, and so affect the weighing. (2) With the old form, on replacing the stopper after tipping out any substance, it is usually found that some substance remains attached to the inside of the neck, thereby getting ground in between the stopper and the neck, causing the stopper to fit inaccurately, and, if left for some time, this makes the stopper stick so firmly that it is generally broken on trying to remove it. The stopper being outside obviates all this. (3) The stopper, when placed on the bench or table, does not roll about, but lies flat. The old form of stopper rolls about, and is likely to have some substance sticking to it, some of which falling off on to the bench, is lost, and affects the weighing. The new weighing-bottle is generally much cleaner to work with. (4) Liquids are more easily dealt with. The bottle may be obtained of Messrs. J. Kerr and Co., Manchester.   W. J. S.

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PRESERVATIVES IN MILK.

The following Circular has been addressed to the various Local Authorities under the Sale of Food and Drugs Acts:

<div align="right">

LOCAL GOVERNMENT BOARD,
WHITEHALL, S.W.
Ju'y 11, 1906.

</div>

SIR,—I am directed by the Local Government Board to request the attention of the Council to the subject of the addition of preservatives to milk.

A serious objection to the use of preservatives in milk has been pointed out in the report of the Departmental Committee on Preservatives and Colouring Matters in Food, who state that preservatives in milk "may be relied on to protect those engaged" in the milk traffic "against the immediate results of neglect of scrupulous cleanliness. Under the influence of the preservatives milk may be exposed without sensible injury to conditions which otherwise would render it unsaleable. It may remain sweet to taste and smell, and yet have incorporated disease germs of various kinds, whereof the activity may be suspended for a time by the action of the preservative, but may be resumed before the milk is digested."

This Committee, after hearing evidence from milk traders, concluded that the addition of a preservative to milk is not necessary for the purposes of the milk trade, even in hot weather of

...ere the supply of so large a place as London is concerned, and the Committee recommended
...at no preservatives should be added to milk.

In making this recommendation the Committee had special regard to evidence received as to
...o classes of preservative substances which, under various names, are frequently used as
...servatives in milk—viz. : (1) Formalin (a 40 per cent. solution of formic aldehyde) and
...her preparations of formic aldehyde ; and (2) boron preservatives (boric acid, borax, or mixtures
...boric acid and borax). The Committee considered that the addition to milk of formalin or
...reparations of formalin, even when the amount which could be detected was minute, was
...jectionable, on account of the alterations effected by formalin in the character of certain of the
...nstituents of milk and of its ability to interfere directly with digestive processes.

Although in the view of the Committee boron preservatives might reasonably be employed
...the case of certain foods, within defined limits and subject to a declaration as to their presence
...d amount, the Committee recommended their exclusion from milk altogether; partly for the
...sons above indicated, and partly also in consideration of the immense importance of pure
...lk for the nutrition of infants, invalids, and convalescents, and of the comparatively large
...antity of milk which may be taken, particularly by children, in comparison with the other
...ds in question. Moreover, the Committee had evidence " pointing to an injurious effect of
...racized milk upon the health of very young children."

Since the report of the Committee was made, the Board have from time to time had before
...m further evidence on the subject, and this supports the conclusions of the Committee not
...ly as to the objections to the use of preservatives on the ground of public health, but also as
...the ability of milk traders to conduct their business without use of preservatives. Thus in
...rtain boroughs in London and elsewhere in which milk samples are systematically tested for
...servatives, the presence of preservatives in milk at any time of the year has been found to be
...ceptional ; and there is evidence to show that a very large number of milk vendors conduct
...ir business without the use of these substances, even where the milk comes long distances
...y rail.

In some districts action under the Sale of Food and Drugs Acts has been frequently and
...ccessfully taken in order to bring about the disuse of preservatives in milk. Proceedings
...stituted against vendors of milk containing preservatives have usually been taken under
...ction 6 of the Sale of Food and Drugs Act, 1875. Conviction has followed, it being held that
...en the purchaser who asks for milk is supplied with milk plus a preservative, he does not
...ceive an article of the nature, substance, and quality demanded, and is prejudiced thereby.

The Board are of opinion that action under the Sale of Food and Drugs Acts in regard to
...servatives in milk is desirable, and that this subject deserves attention from all authorities in
...gland and Wales charged with the execution of these Acts.

In this connection the following suggestions are made for adoption by the Council where a
...milar procedure is not already followed :

1. *Information from Public Analysts.*

The Board suggest that Public Analysts should be requested—

(a) To record in their quarterly reports how many milk samples have been examined
during the quarter with a view to ascertaining the presence of substances commonly
in use as preservatives, and with what result ; and to draw the attention of the
Council to instances where the use of preservatives in milk other than boron
preservatives and formalin have come under notice.

b) To report, on completion of analysis, the facts as to samples of milk which have been
found to contain any added preservative.

2. *Administrative Action where Preservatives in Milk are reported.*

The Board would suggest that the Council should notify to milk traders, by circular otherwise, that action will be taken under the Sale of Food and Drugs Acts in instances wh... preservatives are reported in milk.

Subject to this being done, and to exceptional cases of the kind referred to under heading numbered 3 below, the Board consider that when the presence of any added preservati. is reported in a sample of milk taken in accordance with the provisions of the Sale of Food a. Drugs Acts, the case should in ordinary circumstances be regarded as one for the institution proceedings under those Acts.

3. *Declaration and Notices.*

The Board think it desirable to draw attention to cases in which the vendor of the mil. with the object of escaping liability under Section 6 of the Sale of Food and Drugs Act, 1s7. declares to the purchaser by means of a notice, label, or otherwise, that he does not sell " milk " .. such, or that its quality in regard to preservatives or other constituents is not guaranteed, or th it contains some added preservative.

The Board would suggest the desirability of frequent sampling in cases where " milk " . sold subject to declarations of the kind, with a view to ascertaining the condition of such milk .. regard to preservatives.

The nature of the declaration made should in all cases be carefully recorded by the offic.: taking the sample, and should also be reported to the analyst when the sample is transmitt. for analysis.

Where preservatives are reported in milk thus sold, the question will arise whether, in v.. of the nature and quantity of the preservatives added, it can be considered that the article i.. been rendered injurious to health, or that the purchaser has been prejudiced, to an extent whi. would justify the institution of proceedings under Section 3 or Section 6 of the Sale of Food a: Drugs Act, 1875, notwithstanding the declaration made at the time of purchase.

This question is not without difficulty in view of the general objection to the employment any preservatives in milk referred to above.

As regards formalin and boron preservatives, however, the Board are advised that th presence in milk of formalin to an amount which is ascertained by examination *within three d*, *of collecting the sample* to exceed 1 part in 40.000 (1 part in 100,000 of formic aldehyde) rais a strong presumption that the article has been rendered injurious to health, and that th purchaser has been prejudiced in the above sense ; and also that similar presumption is rais. where boron preservatives are present in milk to an amount exceeding 40 grains of boric ac. per gallon.

It appears desirable that the addition of preservatives to skim milk, separated milk. a: condensed milk should be watched and controlled on similar lines.

Additional copies of this Circular are enclosed for transmission to the Public Analyst. a:' for use by executive officers under the Sale of Food and Drugs Acts. The Circular will be pla. on sale, and copies can then be obtained from Messrs. Wyman and Sons, Limited, 109, Fett. Lane, Fleet Street, London, E.C., either directly or through any bookseller.

I am, Sir,

Your obedient servant,

S. B. Provis,

Secretar.

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REVIEWS.

STUDIES ON IMMUNITY. By Professor PAUL EHRLICH and his Collaborators. Translated by Dr. CHARLES BOLDUAN. (New York: John Wiley and Sons. London: Chapman and Hall, 1906. Pp. 586. Price 25s. 6d. net.)

Ehrlich's studies on immunity have acquired a world-wide reputation, and all investigators in this important field of study will welcome an English translation of the work of himself and his collaborators. In his preface the author points out that Behring's great discovery of antitoxin opens new paths for research, first in the direction of the production of individual curative sera, and, secondly, in seeking a deeper insight into the nature of immunity phenomena.

Ehrlich's theories are developed on the basis of chemical conceptions, and he shows that the significance of morphological structure is far less than that of the chemistry involved. By a comparison with the mechanical conditions and suitable apparatus that aid, but are not absolutely necessary to a chemical process that depends essentially on the constituents involved, so in biology the morphological arrangement of the organs and cells is not the essential feature. This is rather to be sought for in chemical differences of the constituents.

The products of bacteria, as well as the artificially-produced bacteriolysins and most of the ferments, according to the author, produce their effects by the presence of two active groups in the molecule, one of these uniting with the substance to be acted upon, whilst the other produces the characteristic effect. This theory is bound to affect the study of vital phenomena, especially intracellular metabolism and other physiological problems, such as those of secretion, heredity, etc.

The book comprises forty-one chapters by various investigators on the subject of immunity, including many by Ehrlich himself.

One of these is of special interest from the chemical standpoint, consisting as it does of a discussion of the relations existing between chemical constitution, distribution, and pharmacological action. The author here shows that at the present time the chemical aspect constitutes the axis about which the most important views in medicine turn, and that the two poles are the synthetic construction of new therapeutic agents on the one hand, and the discovery of specific therapeutic products of living cells on the other.

He also enumerates the conclusions that can be drawn from the study of the large number of medicaments of therapeutic importance. In this synopsis the fact is emphasized that the antipyretic power of antipyretics is destroyed by the introduction of salt-forming acid radicals, such as SO_3H and $COOH$, and cites as an illustration of this acetanilido-acetic acid ($C_6H_5N(COCH_3)CH_2COOH$), and acetanilin sulphonic acid ($C_6H_5NH.CO.CH_2.SO_3H$), which are inert in this respect.

Ehrlich also mentions that the presence of the ethyl group in certain disulphons —for example, sulphonal [$(CH_3)_2C(SO_2C_2H_5)_2$] and trional [$CH_3C_2H_5C(SO_2C_2H_5)_2$], as shown by Baumann—gives to these substances their hypnotic property, and that the latter increases with the number of these groups.

Another interesting chapter is that by Dr. Preston Kyes and Dr. Hans Sachs on the substances which activate cobra venom.

The book is well arranged, and should prove of great interest and value to all students and workers in the important subjects of immunity and vital phenomena.

OFFICIAL CHEMICAL APPOINTMENTS. By R. B. PILCHER. (London: Institute of Chemistry. Price 2s. net; post free, 2s. 3d.)

Whilst the clerical, legal, and medical professions have been long since well supplied with copious directories, giving, amongst other things, lists of appointments held by members of each respective profession, no approach to such convenient works of reference has been hitherto compiled for the chemical profession. In order to fill up this void, Mr. R. B. Pilcher, the able Registrar of the Institute of Chemistry, has under the direction of the Council of that body and under the supervision of its Proceedings Committee, undertaken the compilation of such a work. The list of official appointments is in two divisions, the former embracing the holders of appointments in Great Britain and Ireland, the latter of those in our colonies; that of appointments held by Public Analysts, which was published some months since, has also been incorporated with the work. In order to be as comprehensive as possible, appointments in connection with agriculture, metallurgy, assaying, and other branches of work where chemical knowledge is required are mentioned. In many instances particulars are given as to the Acts under which appointments are made, as well as the regulations and conditions of such appointments. The work also contains a large quantity of useful miscellaneous information on many subjects.

Mr. Pilcher is to be congratulated on the excellent manner in which he has performed his arduous task; he has succeeded in producing a very useful and highly interesting book for members of the profession to whom it relates, as well as to many outside that profession. 　　　　　　　　　　　　　　　　　W. J. S.

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INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

PASS LIST OF THE JULY EXAMINATIONS.

OF fourteen candidates who entered for the Intermediate Examination, the following nine passed: L. C. W. Bonacina, W. R. S. Ladell, D. J. Law, W. M. Seaber, B.Sc. (Lond.), P. Stutfield, J. M. Weir, M.A., B.Sc. (St. Andrews), W. A. Whatmough, J. M. Wilkie, B.Sc. (Lond.), and C. H. Wright, B.A. (Cantab.). In the Final Examination for the Associateship (A.I.C.), of three examined in the branch of Mineral Chemistry, two passed: J. W. Agnew and I. M. Heilbron. Of three in the branch of Organic Chemistry, two passed: R. Le Rossignol, B.Sc. (Lond.), and G. W. Monier-Williams, M.A. (Oxon.), Ph.D. (Freiburg). And of eight who entered in the branch of the Analysis of Food and Drugs and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy, the following six passed: J. G. Annan, B.Sc. (Lond.), C. T. Bennett, B.Sc. (Lond.), G. W. Glen, F. W. Harris, E. H. Merritt, B.Sc. (Lond.), and F. Tattersfield. The Examiners in Chemistry were Mr. W. W. Fisher, M.A. (Oxon.), F.I.C., and Dr. G. G. Henderson, M.A. (Glasgow), F.I.C. The Examination in Therapeutics, Pharmacology, and Microscopy was conducted by Dr. F. Gowland Hopkins, M.A. (Cantab.), F.R.S., F.I.C.

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

ON THE EXAMINATION OF OLIVE, LINSEED, AND OTHER OILS.

By R. T. THOMSON and H. DUNLOP.

(Read at the Meeting, June 14, 1906.)

HAVING seen reason, after careful investigation, to adopt Wijs' method of determining the iodine value of oils in place of the Hübl method, we have made an examination of various oils of undoubted genuineness, and propose in the present paper to describe the results. As we have stated before, there is an element of uncertainty and unreliability in the Hübl method, and in any event the Wijs and Hübl results cannot be depended on as being interchangeable. It is therefore of importance that a fresh series of iodine values by the Wijs method should be constructed, and this we have done for several oils in the present paper, and embodied the results, along with those of other constants, in Tables I. and II., p. 282.

In the case of the olive oils prepared from the olives by ourselves, those extracted by carbon bisulphide were from the residue left after pressing out the bulk of the oil, and it will be observed that there is little difference between the two varieties. It is evident from these results that a genuine olive oil may vary in iodine value from 81 to 89, and may be regarded as such if the other constants are normal. There is a peculiarity with regard to the Mogador oil, which has an extremely high iodine value, while the refractometer reading is lower than would be expected. We have found with regard to linseed and fish-liver oils that the iodine value and refractometer reading practically rise and fall simultaneously, but olive oil appears to be quite erratic in this respect, as will be seen by an inspection of the tables. This difference is no doubt partly due to the influence of the free fatty acids, which, it has been stated, lower the refractive power; and this is undoubtedly the case, as will be seen from Table III., p. 283.

TABLE I.

Oils extracted by ourselves from the Seed or Fruit, so that their Genuineness can i. absolutely depended upon.

	Iodine Value (Wijs)	Zeiss Refracto- meter at 25° C.	Saponifi- cation Value. Per Cent.	Unsa- ponifiable Matter. Per Cent.	Specific Gravity, 60° F.	Free Aci. P. Cen.
Olive oil (Spanish, green, by pressure)	83·20	61·2	19·56	1·25	—	1·28
Olive oil (Spanish, green, by CS₂)	83·20	61·2	19·21	1·62	—	0·90
Olive oil (Spanish, ripe, by pressure)	88·95	61·3	19·28	1·34	0·9156	0·51
Olive oil (Spanish, ripe, by CS₂)	88·15	62·2	19·14	1·52	—	0·36
Olive oil (Turkish, very ripe)	89·1	61·2	19·21	1·24	0·9156	9·37
Linseed oil (Riga seed)	205·4	85·5	19·21	1·25	—	—
Linseed oil (St. Peters- burg)	200·0	84·2	19·28	1·23	—	
Linseed oil (North American)	194·6	83·2	19·21	1·10	—	—
Linseed oil (Calcutta) ...	188·6	81·7	19·28	0·88	—	.
Linseed oil (River Plate)	185·5	81·0	19·14	1·25	—	—
Ravison oil	118·1	71·0	18·13	1·65	—	
Jamba oil ...	98·3	67·2	17·53	1·02	—	
Rape oil (East India) ...	104·5	68·0	17·53	1·02	—	
Almond oil	98·1	64·3	—	—	—	
Castor oil	85·6	78·3	18·16	0·60	—	

TABLE II.

Oils obtained from Reliable Sources.

	Iodine Value (Wijs).	Zeiss Refracto- meter at 25 C.	Saponifi- cation Value Per Cent.	Unsa- ponifiable Matter. Per Cent.	Specific Gravity, 60° F.	Free Acid. P. Cen.
Olive oil (Crete)	81·2	60·2	19·14	—	0·9155	9·40
„ (Italian) ...	83·5	59·7	19·21	—	0·9157	16·01
„ (Sicilian) ...	84·1	60·0	19·07	.	0·9144	11·50
„ (Levant) ...	84·4	61·0	19·21	—	0·9159	9·32
„ (Algerian) ...	85·1	60·7	19·14	—	0·9150	5·62
„ (Syrian) ...	85·3	60·1	19·14	—	0·9145	11·76
„ (Spanish) ...	86·6	61·2	19·21	—	0·9161	7·27
„ (Mogador) ...	94·3	60·5	19·07	—	0·9150	24·72
Poppy-seed oil	140·0	71·0	19·28	0·52	0·9243	1·62
Sunflower oil (Russian) (by Hübl's method) ...	131·3	70·0	18·93	0·70	0·9220	1·21
Arachis oil	87·5	62·6	19·14	—	0·9164	—

TABLE III.

Showing the Effect of Free Fatty Acids on the Refractive Power of Olive Oil.

	Olive Oil (Mogador).	Olive Oil (Italian).
Iodine value before removal of free acid	94·30	83·50
Iodine value after removal of free acid	93·45	80·45
Zeiss refractometer, 25° C. before removal of free acid	60·50	59·70
Zeiss refractometer, 25° C. after removal of free acid	63·40	61·00
Free oleic acid, per cent. before removal of free acid	24·72	16·61
Free oleic acid, per cent. after removal of free acid	0·32	0·27

TABLE IV.

Comparison of Iodine Value and Refractive Power of Linseed and certain Fish-liver Oils.

	Iodine Value.	Zeiss Refractometer at 25° C
Linseed oil (Riga)	205·4	85·5
„ (St. Petersburg)	200·0	84·2
„ (North America)	194·6	83·2
Skate-liver oil	191·4	82·5
Linseed oil (Calcutta)	188·6	81·7
Haddock-liver oil	186·4	81·0
Linseed oil (River Plate)...	185·5	81·0
Whiting-liver oil	184·2	81·0

The differences referred to cannot, however, be entirely explained by the influence of the free acid, as will be apparent from an examination of the results in Tables I. and II., and especially of those of the two oils extracted from the same Spanish ripe olives, where the oil with the lower iodine value shows the higher refractive power, the free acids being practically the same.

The different samples of linseed from which we prepared the oils were carefully examined, and any foreign seeds removed, so that only the genuine linseed was employed. It will be observed that the iodine value for the oil extracted from the Riga seed is, we believe, the highest on record, while that from the River Plate has an iodine value much higher than what was recorded by one of us some years since. There can be no doubt, however, that these high figures are due partly to the use of the Wijs in place of the Hübl method, and where the former is employed any iodine value below 180 should lead to a more searching examination of the oil.

As regards the other oils of which the constants are included in the tables, it is scarcely necessary to make any remarks, except that the jamba oil cannot be distinguished from rape oil by ordinary means, and that in some few cases the

employment of the refractometer along with the iodine value may be useful, although the former is of no independent importance.

In conclusion, we would draw particular attention to the peculiar similarity between various linseed oils and certain fish-liver oils as regards iodine value and refractive power, as shown in Table IV., p. 283.

Of course, linseed oils have a distinctly higher specific gravity than the fish-liver oils, but the saponification value and unsaponifiable matter are much the same in each.

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ON THE COMPOSITION AND VALUATION OF OILS USED FOR GAS-MAKING PURPOSES.

By RAYMOND ROSS, F.I.C., AND J. P. LEATHER.

(Read at the Meeting, June 14, 1906.)

A LARGE number of investigations have been made by numerous workers into the composition of the various petroleum oils found in certain parts of the world. These investigations have been largely confined to the fractions of low boiling-point, and their principal aim has been the separation and isolation of definite compounds.

The aim of our work has been primarily directed to the valuation of those oils which are used for gas-making purposes. Such oils consist generally of those portions of the crude oil which boil between 200° C. and 400° C. In certain states of the oil market even the refined petroleum burning oils are also used.

From the results obtained by previous investigators—to which we shall refer later—we know that the various classes of hydrocarbons are found in varying proportions, according to the origin of the oil.

This being the case, it is evident that to obtain a satisfactory knowledge of the gas-making properties of any oil, it is necessary to ascertain the proportion of the different classes of hydrocarbons present in the oil, and the gas-making properties of each class. The presence of the following classes of compounds in given petroleum oils has been proved by various workers—notably, Markownikoff, Zelinsky, Aschan, Schorlemmer, Engler, Schutzenberger, Maybery, and others :

Paraffins.
Olefines.
Aromatic hydrocarbons.
Naphthenes.

In this last term are included saturated and unsaturated hydrogenated derivatives of both benzene and naphthalene and their homologues. Some preliminary work which we undertook—the result of which was communicated to the Society of Chemical Industry (May, 1902)—led us to think that the determination of certain chemical and physical properties of an oil might enable a correct judgment to be

formed of the nature and composition of any gas oil. For this purpose it was necessary that the physical properties and the value for gas-making properties of each class of hydrocarbons should be separately determined. The present communication sets forth the progress that we have so far made in this direction, and also the results obtained from the examination of a large number of gas oils.

Although, owing to the difficulties inherent to such a research, our progress is more limited than we had hoped, we trust that our results will be found to be both of theoretical interest and practical utility.

Before proceeding further it will perhaps be best to recapitulate the methods which we use for the valuation of an oil, and which are substantially those mentioned in our previous paper.

For the purpose of gasifying the oil we make use of a retort about 9 inches long by 5¼ inches wide and 1¾ inches in height. This is heated in a muffle furnace. The retort carries an electrical pyrometer and two tubes—one for introducing the oil, going only a short distance into the retort, and the other for the exit of the gas, being carried the whole length of the retort.

The oil is fed in from a burette, and the gas, after passing through a tar-bottle, is collected in a holder, measured, and analysed. After the retort has been brought to the required temperature, the gas-supply is turned off, and 15 c.c. of oil run in during a period of about three minutes.

Experience has shown us that if these directions are followed there is practically no variation in the temperature of the retort during the period of gasification. The size of the retort as well as the rate of flow of the oil are important factors, as if the time of contact is altered, the quantity and quality of the resultant gas are affected. The resultant gas is measured, and then the amount of hydrocarbons absorbed by fuming sulphuric acid is ascertained in a Hempel burette, and this figure is given in all our results as "hydrocarbons."

The number of c.c. of gas at N.P.T. per c.c. of oil (at 15° C.), multiplied by the percentage of hydrocarbons ascertained as above, gives a number which we have called the "valuation figure." The temperatures which we have selected for cracking the oils are those at or between which we have, after many experiments, invariably obtained the highest valuation figure.

In addition to the foregoing cracking test, we make a distillation test on the following lines: 250 c.c. of the oil are distilled, and the fractions are separated at intervals of 20° C. in such a way as to have an even number for the second digit. The quantity of each fraction is measured, and its specific gravity and refractive index determined. The specific refraction is then calculated. Before proceeding further it will, perhaps, be best to give a résumé of the results which we have obtained by the examination of a number of different oils from various parts of the world.

DISTILLATION TEST.

AVERAGES OF GASIFICATION RESULTS.

Name of Oil.	Temperature of Cracking	C.c. of Gas N.T.P. per c.c. of Oil.	Hydrocarbons per Cent.	Valuation Figure.
Pennsylvanian ...	1260° F.	445	35·8	15,944
	1400° F.	529·9	30·1	15,950
	1510° F.	563	26·6	14,967
Kansas ...	1260° F.	438·9	33·6	14,717
	1400° F.	482·6	28·4	13,706
Russian ...	1260° F.	465·7	34·2	15,927
	1510° F.	556	22·8	12,677
Russian refined ...	1260° F.	429	31·8	13,642
	1510° F.	518	28·4	11,711
	1700° F.	550	21·5	11,825
Texas ...	1130° F.	325	30·1	9,769
	1260° F.	388·3	29·8	11,490
	1400° F.	461·8	25·3	11,697
	1450° F.	547·7	18·6	10,187
	1510° F.	508·8	21·1	10,711
Californian ...	1130° F.	370·8	29·8	11,050
	1260° F.	529·9	26·6	14,095
	1400° F.	573·9	25·4	14,577
Roumanian ...	1130° F.	301·3	40·5	12,302
	1260° F.	388·8	33·3	12,895
	1400° F.	459·7	28·6	13,147
	1450° F.	557·3	20·2	11,257
Galician ...	1260° F.	452·8	35·5	16,074
Grosny ...	1130° F.	341·8	34·9	11,925
	1260° F.	421·9	34·6	14,489
	1400° F.	501·6	25·8	12,860
Borneo ...	1260° F.	301	26·8	8,067
	1510° F.	172	17	8,024
	1640° F.	495	15	7,425
Scotch ...	1130° F.	286·5	10·3	11,548
	1260° F	426·4	34·2	14,620
	1450° F.	491·5	26·1	12,790

As the worst results which we have obtained were got from Borneo oil, we determined to make a special examination of this oil.

We commenced work on the lower boiling fractions with an attempt to obtain some definite compound by means of repeated fractional distillations, but without success. We therefore had recourse to chemical means, and to this end treated that fraction of the oil which boiled in the neighbourhood of 200° C. with an excess of fuming nitric acid for a period of some days with constant mechanical stirring, adding the nitric acid gradually, and warming when the violence of the reaction had abated. At the end of the time the mixture separated into three layers—viz., unacted on oil, a wax-like substance, and nitric acid. The residual oil was treated with sulphuric acid and then heated with fuming sulphuric acid (50 per cent. SO_3) severa

times. It has been shown that fuming nitric acid acts in the following manner (Francis and James, *Chem. Soc. Journ.*, 1898)—viz., it readily attacks aromatic compounds, methyl derivatives of polymethylene compounds, and the iso-paraffins. All these compounds are characterized by the presence of a CH group. Consequently in the fraction experimented upon only normal paraffins and decahydronaphthalene could be present in any quantity after the double treatment. An analysis of the remaining oil gave the following figures :

Per Cent.

$$\left. \begin{array}{cc} C & 86.27 \\ H & 14.13 \end{array} \right\} \text{Specific gravity of oil, } 0.821 \ 15°/15°$$

This analysis shows less hydrogen than corresponds to C_nH_{2n}, and it therefore approximates more nearly to decahydronaphthalene than to a paraffin.

The oil was next boiled with excess of bromine in carbon tetrachloride with a reflux condenser for many hours, in the hope that some substitution might take place in the paraffins. Hydrobromic acid was given off, and after distilling off the carbon tetrachloride, the residue was boiled with caustic soda to decompose the bromine compounds and thus leave unsaturated products. After washing, the oil was again treated with fuming sulphuric acid and warmed. After separation, washing, and drying, the oil gave on analysis :

Theory for $C_{10}H_{18}$.

$$\begin{array}{ccccc} C & 86.77 & \dots & \dots & 86.96 \\ H & 13.24 & \dots & \dots & 13.04 \end{array}$$

Its specific gravity was 0.843 at 15° C. The N_D 1.4507. Boiling-point, 169.5° C. Molecular weight determination by Beckmann's boiling - point method, 133 (theory 138). According to Beilstein the gravity is 0.847 at 15° C., and the boiling-point 173° to 180° C. The substance obtained, which was probably fairly pure deca-hydronaphthalene, was then cracked in a similar manner to the gas oils at 1260° F., and gave results as below :

434.1 c.c. of gas at N.T.P. per c.c. of oil containing 26.2 per cent. of hydrocarbons soluble in fuming sulphuric acid, giving a valuation figure of 11,373.

The yellow wax-like substance obtained by nitrification was washed, separated, and dissolved in absolute alcohol. After many attempts two batches of crystals were obtained, in which the carbon was estimated by moist combustion with chromic acid. Several ordinary combustions were spoilt by explosions, even when air was used and great care exercised. The gas from the moist combustion was led through a combustion-tube containing copper oxide and reduced copper. The first batch of crystals gave, as a result of three closely agreeing analyses, carbon 54.28 per cent., and the nitrogen, as determined by the modified Kjeldahl method, was 12.7 per cent. These figures point to a dinitrotetrahydronaphthalene, for which the theory is $C = 54.04$ per cent. and $N = 12.61$ per cent. To verify this suggestion we treated about 70 grams of the nitro compound with 300 grams of tin and 1 litre of hydrochloric acid, heated under a reflux condenser until the tin was dissolved; we then added an excess of strong caustic soda. A thick, pitchy mass rose to the top. This was washed with water and finally distilled *in vacuo*.